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AN ACCOUNT  
OF THE MOST IMPORTANT  
RECENT DISCOVERIES AND IMPROVEMENTS  
IN  
CHEMISTRY AND MINERALOGY,  
TO THE PRESENT TIME;  
BEING AN  
APPENDIX  
TO THEIR  
DICTIONARY OF CHEMISTRY AND MINERALOGY,

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By A. & C. R. AIKIN.

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R. A. & C. R. ALLEN

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IN the following pages (intended as an APPENDIX to their Dictionary of CHEMISTRY AND MINERALOGY) the authors have endeavoured to give a perspicuous and sufficiently detailed account of the various and highly important discoveries by which the science has been enriched during the few years that have elapsed since the publication of their former volumes.

Considerable pains have been taken in verifying calculations; in collecting valuable but diffused information into one focus; in stripping it of the occasional acerbity of controversy; and in moulding the whole to that form of practical utility, which may best secure it from being superceded by future discoveries.

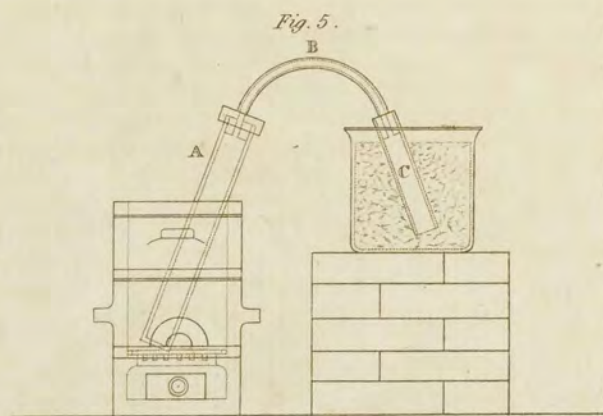
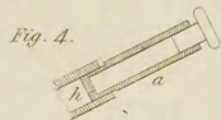
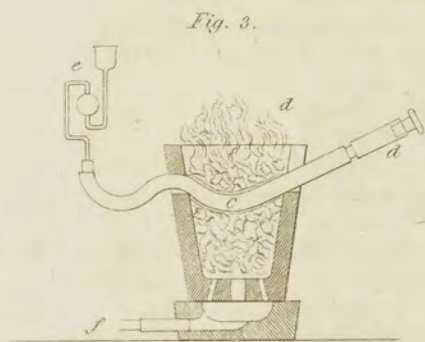
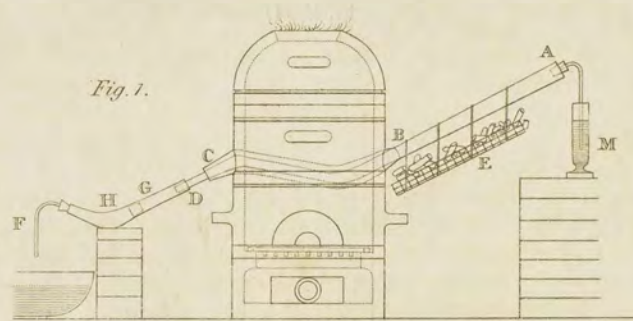
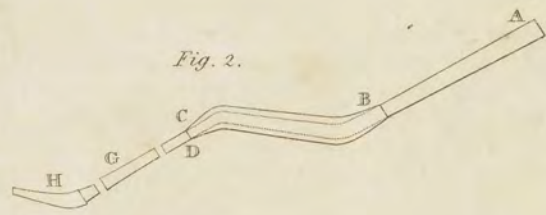
We trust that the purchasers of the Dictionary will not find the present Supplement unworthy of their notice.

In the following paper I attempt to show that the  
Theory of Continuity (and its extension) is  
more or less a truism and a necessary detail  
and right to present theories of which the science has  
known for a few years that have placed the public at a distance

Continuity has been taken in various  
colours and shades for the last hundred years and has  
the essential nature of continuity, and in proving the whole in the  
form of partial truths which are not to be taken as a whole

We must then be prepared to find that the  
present judgment is not of that nature





p. 1

A

A C A

**ACANTICONE.** See AMPHIBOLE.

**ACETIC ACID. ACETITES. VINEGAR.**

M. Cadet<sup>a</sup> has made several experiments on the manufacture of sugar-vinegar and the best proportions of ingredients. It is well known that pure sugar dissolved in water will not ferment by itself; but if yeast or leaven be added, fermentation is soon established, at first vinous, afterwards acetous. Mucilage, Extract, Fecula contributed materially to the products of fermentation, but M. Cadet has apparently been compelled in order to simplify the enquiry, to pass over very slightly the effects of these substances, and to confine himself to the operation of sugar alone. His results therefore can only be considered as affording some approximation to accuracy. To form a simple sugar vinegar he gives the following as the best proportions.

Sugar . . . . .	12.4.
Leaven or Yeast . . . . .	8.
Water . . . . .	86.8
	100.0
	----

When a much greater proportion of sugar is added, a portion of it escapes fermentation, and may be procured from the vinegar unaltered. Though alcohol is the leading product of the vinous fermentation, and therefore (*ceteris paribus*) the more alcohol a fermented liquor contains, the greater quantity of acetous acid it will produce, yet the addition of alcohol to the fermenting liquor will not encrease the product of acetous acid, and if more than about  $\frac{1}{7}$  of

A C E

alcohol be added, the fermentation is entirely stopped and no vinegar is formed.

In making vinegar in the large way, from whatever vegetable material, whether wine, cyder, grain, carrots, sugar, &c. M. Cadet advises a previous essay of about 8 ounces of the material (if dry) with 3 pounds of water and  $\frac{1}{2}$  oz. of yeast fermented completely into vinegar. To this is to be added gradually a solution of caustic potash of known strength, till the liquor is saturated (as determined by litmus, &c.) and the quantity of solid potash noted. Then for every part of potash used he estimates 1.268 parts of sugar to have been acidified by the fermentation, and hence the saccharine strength of the materials is found. Then to produce the strongest possible vinegar without leaving any undecomposed sugar, he proposes so much sugar to be added to the materials (if deficient in this principle) as will raise the proportion to 12.4 per cent. of the whole fermenting mass, which (with the 0.8 per cent. of leaven) produces as above mentioned the most favourable proportions for this manufacture.

The density of acetic acid cannot be depended on singly as any indication of the *strength* of acidity. On this subject M. Mollerat has some valuable observations.<sup>b</sup> The strongest acetic acid that he could obtain, which was quite pure and free from empyreuma, had the specific gravity of 1.063 at 60° Fahr. This was highly volatile when moderately heated, and entirely congealed at about 55°, and did not thaw at 72°. A given portion of it saturated 250. of carbonat of soda, and its proportion of real acid

<sup>a</sup> An. Chim. tom. 62.

<sup>b</sup> Ibid. 68.

was reckoned at 87.125 per cent. A mixture of the same acid and water in a certain proportion was made, which had exactly the same specific gravity, but its saturating power was only equal to 118 of carbonat of soda, or 58.725 real acid. A further addition of water to this last acid *diminished* the density as well as the saturating power, and this continued uniformly in every subsequent proportion of water added. On the other hand the first addition of water to the concentrated acid of 1.063 sp. gr. *increased* the specific gravity, though the proportion of real acid was of course diminished. Hence there must be a point of the maximum of specific gravity in which the gravity would be lessened both by encreasing and diminishing the real strength of the acid as measured by its saturating power. This maximum of density M. Mollerat estimates at 1.0791 sp. gr. and 67.256 per cent. of real acid.

The observations of M. Derosne, M. Berthollet and Mr. Chenevix, which we shall presently mention, confirm this fact of a maximum density existing in this acid in a certain state of dilution. These observations however only apply to the acetic acid or *radical vinegar* obtained from some of the neutral acetates. The common distilled vinegar contains a quantity of carbonaceous matter which can only be separated by combining it with a basis and redistilling it.

Mr. Chenevix<sup>c</sup> has given a valuable experimental essay on acetic acid and some of the acetates. A quantity of acetite of copper was distilled *per se*, and the product separated as it came over into different portions. The first portion had the specific gravity of 1.0659, and the proportion of real acid estimated from its saturating power was 62.971. The second was 1.058 sp. gr. and 67.461 acid: the third, 1.0454 sp. gr. and 74.411 acid; the fourth, 1.040 sp. gr. and 73.295 acid.

Though these numbers do not exactly correspond with those of M. Mollerat, they shew that the specific gravity of acetic acid is no indication of its strength in real acid, and the reason of this is supposed to be the admixture of a portion of an inflammable spirit in various proportions formed during the distillation of the acetites, which has been examined by various chemists, and which the author terms *Pyro-acetic Spirit*; and M. Derosne, *Pyro-acetic Ether*.

The products of the distillation of the metallic, alkaline and earthy acetates differ remark-

ably in the proportions of the acid, pyro-acetic spirit, and gaseous products, though the acetates themselves are all prepared with the same acetic acid. Hence it becomes an interesting enquiry to examine what is the action of these bases on the acid during distillation, which can explain this great difference in the products. The analysis is complicated and attended with many difficulties, but the experiments of Mr. Chenevix on this subject deserve notice. The metallic acetates examined were those of silver, copper, nickel, lead, iron and manganese. A given quantity of each was distilled from a luted earthen or glass retort according to the heat required, to which was attached a tubulated matrass to collect the liquid products, a Woulfe bottle holding a solution of pure barytes, and a pneumatic trough. The heat was kept up as low as possible to effect the decomposition. The results consisted therefore of three substances which required a subsequent examination, namely, the metal or metallic oxyd left in the retort, the liquid, and the gaseous products. The metallic residue was reguline in some cases and oxidated in others, and mixed with a small portion of charcoal which was separated by dissolving the metal.

The liquid product was examined in relation to its specific gravity, its acidity, and the quantity of pyro-acetic spirit. The force of acidity was measured by the quantity of a solution of pure potash saturated by a given portion of the acid. It was more difficult to separate the pyro-acetic spirit. When alcohol is mixed with any watery liquid, the usual mode of detecting it is by the addition of carbonate of potash, but where the liquid also contains an acid which by union with potash forms a salt soluble in alcohol, this mode of separating the spirit will not answer. It was therefore necessary in the present instance to redistill from potash the liquid products of some of the acetates, and thus deprive them of their acid, before the spirituous portion could be obtained. We shall add the results of these experiments as far as concerns the liquid product in the three circumstances of specific gravity, acidity and spirit.

	Sp.Gr.	Acidity	Spirit
Acetite of Silver .	1.0656	107.309	0.
Acetite of Nickel .	1.0398	44.731	2.
Acetite of Copper .	1.0556	84.868	0.7
Acetite of Lead .	.9407	3.045	0.555
Acetite of Iron .	1.011	27.236	0.24
Acetite of Zinc .	.8452	2.258	0.695
Acetite of Manganese .	.8264	1.285	0.94

<sup>c</sup> An. Chim. tom. 69.

Of these acetites the metallic bases of the four first were left after the process in the reguline state, the iron was the black oxyd, the zinc the white oxyd, and the manganese the brown oxyd. The enormous difference in strength of acidity which these products shew, must immediately strike the reader. The author inclines to the opinion that in proportion to the greater difficulty of the reduction of the metallic base is the quantity of spirit yielded and of acid destroyed. Thus the acetite of silver which is reduced with the greatest ease, gives an acid of much greater strength than the others, but no ascertainable quantity of spirit. On the other hand the acetite of lead, which is reduced with more difficulty, and the acetite of zinc which is not reduced at all, give a very weak acid but more spirit. It must be acknowledged however that the production of spirit bears no proportion to the destruction of acid, so that no argument can be hence derived of the conversion of the latter into the former.

When the acetites of potash and of soda are distilled *per se*, they yield a more spirituous and less acid product than any of the metallic acetites. The product from dry acetite of barytes had the specific gravity of only .8458, did not redden vegetable colours, but contained so concentrated a spirit that it was necessary to add water to enable carbonat of potash to produce any separation of spirit, and then the quantity of spirit separated was more in bulk than the entire original product of the distillation. Hence the spirit was in a more condensed state before, than after the separation. Mr. Chenevix has found the acid product distilled from acetited silver to contain the purest and strongest acetic acid and the least mixed with spirit. Its specific gravity was 1.0656 when undiluted, and its saturating power estimated at 107.309. When gradually lowered by water, the specific gravity at first *increased* to 1.0733, but after this point again *diminished* by every subsequent dilution. This anomaly in the change of specific gravity cannot be accounted for *here* by the presence of pyro-acetic spirit, since none was detected, and the author therefore ingeniously attributes it to the strong tendency of crystallization at a moderate temperature, which this very concentrated acid possesses, and which probably acts as it does with water to produce an expansion of the liquid as it cools down to its point of congelation. The fact of the ready crystalli-

zation of the acid is undoubted, and this appears not to be owing to the presence of any spirit or extraneous matter, but rather to depend on the degree of concentration of the acid itself.

It has been maintained by some chemists that prussic acid and ammonia are among the products of the distillation of the acetates. This however is denied both by Mr. Chenevix and by Tromsdorff. The latter chemist<sup>d</sup> distilled acetite of soda, acetite of lead and acetite of potash, separating the volatile portion from the residue. The former was passed through an ignited tube, and carbonic acid, carburetted hydrogen and empyreumatic oil were produced, but no prussic acid nor ammonia appeared either in this or in the fixed residue.

The latest analysis of acetic acid that we possess, is one of a very interesting series on various animal and vegetable substances, performed by Messrs. Gay-Lussac, and Thenard.<sup>d</sup> The mode of analyzing is original, being by combustion with oxymuriat of potash, as will be further described under the article ANALYSIS. The acetic acid was procured from acetite of potash by sulphuric acid, without any artificial heat, and the acid obtained was quite free from any admixture of the sulphuric. It was first boiled with carbonat of barytes, and the resulting acetite of barytes dried in the heat of boiling water. Thirty grammes of this salt were dissolved in water and decomposed totally by sulphat of ammonia, and the sulphat of barytes, when ignited, weighed 25.445 grammes, of which the barytes, according to the received proportions, forms 67 per cent. and hence the composition of the acetited barytes dried at a boiling water heat, is 43.17 per cent. of acetous acid, and 56.83 barytes.

This acetite was then ignited with oxymuriat of potash, and the acetic acid when reduced to its ultimate elements, carbon, oxygen, and hydrogen, gave the following proportions:

Carbon 50.224, oxygen 44.147, hydrogen 5.629.

Or, supposing all the hydrogen to be united to its saturating proportion of oxygen to constitute water, the result will be,

Carbon 50.224, water 46.911, oxygen in excess 2.865.

Four other vegetable acids were analyzed by these chemists in the same manner, namely, the oxalic, the mucous, the tartaric, and the citric, and the general results are as follow:

<sup>c</sup> An. Chim. tom. 58.

<sup>d</sup> Recherches Physico-Chimiques, &c. tom. 2.

	Oxygen in each.	Carbon.	Water.
Oxalic	50.56	— 33.57	— 22.87
Mucous	36.15	— 33.69	— 30.16
Tartaric	20.71	— 24.05	— 55.24
Citric	13.44	— 33.81	— 52.75
Acetic	2.87	— 50.22	— 46.91

These analyses, if correct, give a totally different idea of the constitution of the acetic acid, compared with the other vegetable acids, from that usually entertained. It has been maintained by Westrumb, Hermbstaedt, Crell, and others, that the pure acid of vinegar was the ultimate term of oxygenation of all the vegetable acids, so that any other of these could be converted into the acetic by an oxygenating process. Thus Hermbstaedt converted the dry acid of tartar entirely into the acetous, by distillation with manganese and sulphuric acid. (*See article Acetous Acid, Ch. Dict. vol. 1, p. 4.*) But on the other hand the above experiments of Messrs. Gay-Lussac and Thenard shew that the acetic acid is by far the *least* oxygenated of the five vegetable acids here mentioned, but contains a much larger proportion of carbon, and hence one may expect the acetic acid to be among the *earliest* products of any acidifying process going on in vegetable matter. This, they maintain, is supported by actual observation, for the acetic acid is that into which all vegetable and even animal matter is the soonest changed, whether by distillation or the putrid fermentation, or by the action of the nitric and sulphuric acids. How, say they, should these changes take place (especially that of wine into vinegar) and no intermediate acid be found, if the acetic acid was the most oxygenated.

#### *Pyro-Acetic Spirit. Pyro-Acetic Ether.*

This substance having already been partially described in our account of Mr. Chenevix's experiments, and also having been previously examined by Derosne,\* we shall here add some further notice of it. It is contained, as already mentioned, in the product of the distillation *per se*, of most of the acetites, and it is probably in many cases owing to the admixture of this spirit that the specific gravity of the distilled liquid is so much lessened as to counteract the increased density which would naturally arise from a great intensity of acid. M. Derosne obtained it in the following experiments, which were also undertaken as a general examination of the products in the usual way of preparing acetic acid. An earthen retort was filled with

41½ lbs. (French) of verdigris, and distilled *per se*, in a very gradual heat kept up for three days. The products were divided into four successive portions, each of which was kept separate. The first portion weighing 5 lbs. 10 oz. was weakly acid to the last, and of a slight blue colour.

The second was stronger and deeper coloured, and weighed 6 lbs. 4 oz.

The third, was still stronger and more blue, had a much more pungent smell, but rather empyreumatic. It weighed 7 lbs. 4 oz.

The fourth was slightly yellow, had a weak but very empyreumatic smell, and required a very strong heat to be expelled. It weighed 8½ oz.

The united weight of these four liquids was 20 lbs. 5 oz. and the cupreous residue in the retort weighed 13 lb. 14 oz. so that there was a deficiency of 7 lb. 5 oz. to make up the original weight of the verdigris employed.

A large quantity of gas was produced in the operation, the whole of which was made to pass through a separate bottle of distilled water before it escaped, to which it gave some acidity and a very disagreeable burnt flavour.

The four distilled products were again rectified and divided into successive portions, and by comparing the specific gravity of each with the power of saturating alkali, it was found that the second and third products, or those which were obtained at the middle of the first operation, were much the strongest in acid with the least specific gravity. This intermediate product being rectified at a gentle heat, gave a quantity of inflammable gas, and a light inflammable liquor, but still acid. To separate the acid, solid caustic alkali was added to it in small portions, keeping the vessel in cold water till the acid was saturated, when part of the acetited potash crystallized spontaneously, and a light yellowish liquor rose on the surface, which was carefully decanted and again rectified by distillation at a very gentle heat. The product of this last operation is the *Pyro-Acetic Ether*.

It is quite clear and colourless, its smell pungent, its taste hot and empyreumatic. It is lighter than alcohol, very volatile, and produces cold by evaporation. It is highly combustible, burning with a flame at first blue, afterwards yellowish white. After its combustion it leaves a carbonaceous stain, and if previously mixed with a little water and burned, the water remains slightly acid. It does not

\* An. Chim. tom. 63.



reddén litmus. When added to a solution of gold in nitromuriatic acid with a little dry muriat of lime, the Pyro-acetic ether rises to the surface with a fine golden colour. In all these respects this substance resembles the other ethers, but it differs from them in being miscible with water in any proportion.

Mr. Chenevix, in the memoir already mentioned, has examined this *Pyro-Acetic Ether* or *Spirit* with much care, and compared its properties with those of the true Acetic Ether. To obtain the Pyro-acetic Spirit, acetite of lead was distilled *per se*, in an earthen retort, and the products again rectified, and the spirit separated. Its properties are the following: It is perfectly clear and without colour; its taste burning and somewhat urinous; its smell somewhat resembling that of peppermint mixed with bitter almond. The specific gravity was at first .7929; but after rectification over muriat of lime, .7864. It burns with a white flame, leaving no residue. It boils at 130° Fahr. It mixes with water, alcohol, and the volatile oils, in every proportion; also in some proportions with the fixed oils when cold, and in every proportion when heated. It dissolves a little sulphur, more of phosphorus, and a large quantity of camphor. White wax and fat dissolve in it when hot, but a portion separates on cooling or on adding water. It dissolves a little caoutchouc which is separable again by water, and it renders a solution of gum arabic extremely turbid.

A further examination of this spirit by distillation with potash and with the mineral acids, shews some decided points of difference between the Pyro-Acetic Spirit and the Acetic Ether prepared by acetic acid and alcohol, but a fuller analysis is yet wanting.

Some chemists have attributed the production of an inflammable spirit during the distillation of the acetites to that portion of alcohol which all vinegar contains, and is derived from the vinous fermentation which always precedes the acetous. It is certain that when a large quantity of vinegar is distilled, the first portions contain a little alcohol intimately mixed with the acid. But this alcohol comes over at the first impression of heat, and certainly cannot be supposed to enter into the composition of those solid acetites (verdigris for example) that require long ebullition of the acid and metallic oxyd, and subsequent evaporation to crystallize. Yet it is from these solid acetites that the Pyro-acetic Spirit is prepared, and it rises only towards the middle and end of the distillation,

when a heat much greater than is required to volatilize alcohol has been kept up for a considerable time. This Pyro-acetic Spirit or ether therefore, is obviously a product of the decomposition of some of the component parts of the acetous acid itself, and not an adventitious admixture of alcohol derived from the previous fermentation.

For some further remarks concerning the true acetic ether, see the article *Alcohol* in this Appendix.

#### *Acetate of Alumine.*

Gay-Lussac has some valuable observations on this salt, which are particularly useful to the dyer and calico-printer, who employ a vast quantity of it. When a solution of acetited alumine is heated, it becomes turbid and deposits a great deal of alumine; but (what is very remarkable) all the alumine is gradually redissolved on cooling and agitation. A second heating will again cause the alumine to precipitate, and the liquor will again become clear when cold; and this may be repeated an indefinite number of times. In a neutral solution of acetited alumine (such as is made by the calico-printers, by mixing alum and acetited lead) the author found that the quantity of alumine separated by mere heat was nearly half the whole contents. After the alumine is deposited from the heated solution, the liquor remains with an excess of acid, and hence the necessity of using chalk to saturate this excess, which however is often an injurious addition on other accounts. Alum will prevent this separation of alumine by heat.

ACETIC ETHER and SPIRIT. See the preceding article and ALCOHOL.

ACIDS VEGETABLE. See ANALYSIS.

ACTINOTE. See AMPHIBOLE.

AEROLITE or Meteoric Stone.

That stony masses, sometimes solitary, sometimes in showers, have fallen on the surface of the earth from the upper regions of the atmosphere, is a fact, which, though distinctly and particularly testified both by ancient historians and more modern observers, had gained but little credit among philosophers previously to the last twenty years. On some particular occasions indeed the evidence adduced was so circumstantial and apparently unprejudiced that nothing but the supposed impossibility of the fact prevented its reception. In the mean time new facts bearing a perfect analogy with the preceding ones continued to accumulate, and with such overpowering evidence that all *a priori* arguments gave way before them, and

the existence of atmospheric or meteoric minerals is fully admitted.

In the article *NATIVE IRON*, among the ores of that metal, the reader may find a few details relative to this subject; and a reference to another article *STONES meteoric* which by some unaccountable oversight is wholly omitted. This omission it is the purpose of the present article to supply.

Without adverting to the testimony of Livy, of Pliny, and of other ancient authors, I shall confine myself to a brief enumeration of those aerolites which have either fallen within the last twenty or thirty years, or of which, though the date of their fall is considerably more ancient, specimens are still extant, many of which have of late been submitted to chemical analysis.

Those luminous bodies called meteors or fire-balls, which make their appearance at irregular intervals, traversing with an excessively rapid motion the upper regions of the atmosphere, and ultimately falling on the surface of the earth, appear to be one source of meteoric stones. They evidently consist of a central nucleus in such a state of softness or fluidity as to admit of considerable variations in its shape; sometimes a disruption of the nucleus takes place, accompanied by an explosion, and the two or three pieces into which the mass is thus divided proceed in the direction of their previous course without any apparent abatement of velocity. More usually however the explosion is so violent as to break and disperse the meteor, and the fragments immediately fall to the ground. Of these meteors some of the most remarkable and the best observed in modern times are the following. On the 21st of May, 1676, a meteor was observed by Montanari, professor of mathematics at Bologna, and by others, passing with great velocity across the north of Italy in a direction nearly from E. to W. When it had arrived over the sea to the S.W. of Leghorn it burst with a violent explosion, and its fragments, as they fell into the sea, produced a hissing noise like that occasioned by plunging red hot iron into water.

On the 11th November, 1761, a meteor was observed in several of the provinces of France. It burst with a loud explosion into a great number of fragments in the neighbourhood of Dijon, one of which fell upon a house and set fire to it.

On the 17th July, 1771, a meteor, traversing from N. to S. was observed in England and in France. It burst with a loud explosion S.W.

of Paris, causing a commotion like that of an earthquake. Its elevation above the surface of the earth, when first perceived, was more than 80,000 yards, but at the period of its explosion it had descended to about half its former elevation.

On the 18th August, 1783, a large meteor, traversing in the same direction as the preceding, was observed in various parts of England, of France, and of Italy as far as Rome. When it first was noticed, its apparent magnitude was about equal to that of the planet Jupiter, but it rapidly increased, and at the instant of its explosion was of greater apparent magnitude than the full moon. Its form varied from round to oblong, and an internal movement like that of ebullition was distinctly visible: it divided into several smaller masses, which continued in their onward course before the final explosion by which it was dissipated. The rate of its motion, according to the lowest estimate, was about  $1\frac{1}{4}$  mile in a second.

The diameter of the nucleus of those meteoric bodies is variously estimated at from 100 to 1000 yards; and it is obvious that a body of much inferior size, moving with an equal or nearly equal velocity, would fail to attract notice, especially in the day time, except at the period of its actual explosion. The greater number of instances of the fall of meteoric stones are under circumstances which render it probable that they too are occasioned by the exploding of meteors, which their inferior magnitude alone prevents from being visible. A loud noise, like that of thunder or the firing of heavy artillery, or the overturning of a load of stones, sometimes with, often without any visible flash, is the first circumstance which attracts notice and excites alarm, then a hissing like the noise occasioned by the passage of a shot through the air is heard; a momentary glance of the falling bodies is caught, and they are perceived entering the surface of the soil, the grass and mould being at the same time thrown up on all sides, and a sulphurous odour diffusing itself to some distance around. On immediate search being made, by digging in the direction of these holes, there is found, at the depth of a foot or two, a black roundish stone, sometimes large sometimes small, often too hot to be held in the hand, and smelling strongly of sulphur. Such are the general phenomena; the most remarkable examples are as follow:

1. In the year 1492, according to Sebastian Brandt, there fell from the sky at Ensisheim in

Upper Alsace, a large somewhat oval stone, which from this extraordinary circumstance was kept attached to a chain in the cathedral of that place. The weight of the stone was about 2 cwts. externally it was rough, dull, and of a dark colour. On being broken, it presented a close grained texture and a blackish-grey colour, and contained interspersed confusedly crystallized grains of yellow pyrites, and of grey scaly non-sulphurous iron ore attractable by the magnet, and therefore approaching to the metallic state. The specific gravity of the stone was 3.2: it did not give sparks with steel, and was pulverized without difficulty. It was analyzed by professor Barthold in the year 1797, but this analysis being performed on the entire stone, and not separately on the three substances of which it visibly consists, we can only gather from the result, that it consists of silex, alumine, magnesia, iron, sulphur and a little lime. The conclusion of the professor is, that the stone of Ensisheim is a common argillo-ferruginous mineral, and that its traditionary origin is a mere superstitious fiction.

2. On the 3d July, 1753, a shower of stones, each weighing from one to twenty lbs. and upwards, was said to have fallen during a thunder-storm at Plann near Tabor in Bohemia. One of these was deposited by Baron Born in his cabinet and described in his *Lithophylacium* pt. I. though he considered the account of their origin to be an idle story; and the cabinet of Baron Born coming into the possession of Mr. Greville, the specimen in question was found to form a part of it.

3. On the 20th of August, 1789, a stone 15 inches in diameter fell near Roquefort in the Landes, during the explosion of a meteor. It broke through the roof of a cottage and killed a herdsman and some cattle.

4. In the following year a shower of stones fell in Armagnac.

5. On the 12th July, 1794, about a dozen stones of various weights and dimensions fell in the neighbourhood of Sienna, in the midst of a most violent thunder-storm, at the feet of several persons, men, women, and children. They fell about eighteen hours after the enormous eruption of Mount Vesuvius, but at a distance of at least 250 miles from that volcano. One of the largest of these stones weighed upwards of five lbs. and a piece of this was brought by Sir Wm. Hamilton to England.

6. On the 17th December, 1795, a stone weighing 56 lbs. was seen by several persons to fall near Wold Cottage, in Yorkshire: as it fell a number of explosions were heard. It penetrated through twelve inches of soil and six inches of solid chalk-rock, and in burying itself had thrown a large quantity of earth to a great distance; when the stone was dug out it was warm, smoked, and smelt strongly of sulphur. The stone itself was exhibited in London, and a piece of it was procured by Sir Joseph Banks.

7. On the 19th December, 1798, about eight o'clock in the evening, the sky being perfectly without clouds, a luminous meteor was observed by the inhabitants of Benares in India, and of the parts adjacent, accompanied by a loud noise resembling irregular platoon firing. At a village about 14 miles from the city the natives were alarmed not only by the light and the thundering noise, but with the sound as of heavy bodies falling through the air, and the roof of one cottage was actually broken through by a stone weighing above two lbs. which buried itself to the depth of several inches in the consolidated earth of which the floor was formed. The next morning the inhabitants perceived the ground to be pierced and turned up in various places, and in these on digging to the depth of some inches they found stones perfectly similar in external appearance to that which had forced its way through the roof of the hut. They were of various sizes, from about three inches to upwards of four in their largest diameter. Some of these, with a detailed account of the circumstances above related, were transmitted to England in the following year.

Thus there happened to be at the same time in England specimens from four different parts, viz. from Bohemia, from Sienna, from Benares, and from Yorkshire, of stones said to have fallen from the sky. The date of three at least of these analogous events, was so recent and the circumstantial and direct testimony in their favour was so powerful, that the narrations however extraordinary and however they might separately have been discredited, could not fail of exciting a degree of attention proportioned to their importance. One of the consequences of this was a chemical examination of these four specimens by Ed. Howard, Esq. F.R.S.<sup>a</sup> and an accurate description of their external characters and physical properties by Count Bournon.

The stones from Benares are covered with a thin crust of a deep black colour, without any lustre, and sprinkled over with small asperities which cause it to feel like fish-skin. Internally they are of a greyish ash colour, and of a granulated texture, like that of a coarse grit-stone. They are evidently composed of four different substances. One of these (and that which forms the greatest part of the entire mass) is in the form of distinct concretions, more or less globular, varying in magnitude from the size of a small pin's head to a pea: their colour is grey, inclining more or less to brown, and they are perfectly opaque. They are easily frangible in all directions, and display a compact conchoidal fracture with a slight degree of lustre resembling enamel, the hardness is about equal to that of glass, and they give a few feeble sparks with steel. Another of the substances is reddish yellow iron pyrites, which when pulverized becomes black; it is not attractable by the magnet, and is irregularly dispersed through the substance of the stone. The third substance is iron in minute particles, and perfectly malleable: its proportion to the whole, as estimated from pulverizing the stone and separating the iron by means of a magnet, is about 2 per cent. These three substances are held together by a fourth, which is soft, of an earthy consistence, and a grey colour. The black crust by which the surface of the stone is coated, although of inconsiderable thickness, affords bright sparks when struck with steel, and appears to consist principally of magnetic black oxide of iron. The specific gravity of the entire stone is 3.35.

The stone from Yorkshire presents similar constituent parts with that from India, with the following exceptions. The distinct concretions are smaller, and of a more irregular figure. The proportion of iron pyrites is less; that of the metallic iron is considerably greater, amounting to 8 or 9 per cent. and the iron itself instead of being in minute distinct grains was in irregularly shaped pieces, some of which weighed several grains. The earthy part of the stone has rather more consistence than that of the former specimen, and greatly resembles in appearance decomposed felspar or kaolin. The specific gravity of the stone is 3.5.

The stone from Sienna was black externally, and internally was coarsely granular like the specimen from Benares. Its specific gravity was 3.41. In it might be perceived the same globular concretions, the same kind of iron pyrites, and the same grains of metallic iron,

the proportion of this last somewhat exceeded that afforded by the specimen from Benares. The same kind of grey earthy substance served to connect the different parts together. But, beside the ingredients above mentioned, there were a few globules of black magnetic oxide of iron, and a single globule of a pale greenish-yellow colour; this latter was completely transparent, had a perfectly vitreous lustre and fracture, and in hardness was rather inferior to calcareous spar.

The stone from Bohemia greatly resembles that from Yorkshire. In it may be observed the same grey substance both in globular and irregular concretions, also the same particles of metallic iron, and the same kind of earthy substance connecting together the other parts. It differs however from the others in the particles of pyrites being so small as not to be visible without the help of a lens; and in the proportion of metallic iron amounting to about 25 per cent. of the entire mass. Its specific gravity was 4.28.

The ingredients being the most distinct in the specimen from Benares, was the inducement to Mr. Howard to commence his chemical examination with this. Some pieces of pyrites to the amount of 16 grains being carefully picked out from among the other substances were digested at a low heat with diluted muriatic acid. A small quantity of sulphureted hydrogen was disengaged, and after a time all that remained undissolved was earthy matter to the amount of two grains (thus reducing the real quantity of pyrites operated on to 14 grs.) and about 2 grains of sulphur. The solution was saturated with ammonia, upon which a precipitation of oxide of iron took place, and the supernatant fluid acquired a violet purple colour; this latter, having previously been found to contain not copper but nickel, was decomposed by sulphureted hydrogen. The oxide of iron after ignition weighed 15 grains, and the sulphuret of nickel being reduced to an oxide by calcination weighed something more than one grain. From these data Mr. Howard considers the pyrites as composed of  $10\frac{1}{2}$  iron, 1 nickel and 2 sulphur, estimating the per-oxide of iron to contain 55 per cent. of metal. On examination however it appears that certain difficulties or mistakes adhere to these results, which make the analysis by no means so correct as it appears to be. First, Mr. H. from his own experiments states that 100 parts of iron afford 145 grains of oxide by solution in muriatic acid precipitation by ammonia, and sub-

sequent ignition, hence this oxide contains 70 per cent. of metal, but by the concurrence of Proust, Davy, Thomson, Berzelius and all the best authorities, the per-oxide of iron contains about 52 per cent. of metal, and the protoxide 73 per cent.; hence it is evident that Mr. Howard's oxide was a mixture of the two, and was not sufficiently calcined. Secondly, allowing with Mr. H. that the real quantity of iron was 10.5 grains, this when combined with sulphur in the only two proportions in which it is capable of combining, would produce 16.5 grains of magnetic pyrites, or 21.5 of the common kind. Again, there is the distinct testimony of Count Bournon that the pyrites was not magnetic, and the equally distinct testimony of Mr. H. that it was decomposable by muriatic acid, and that a little sulphuretted hydrogen was at the same time evolved. But of the two known kinds of pyrites the magnetic alone is decomposable by muriatic acid with evolution of sulphuretted hydrogen. We must therefore either suppose some error in the analysis, or that the pyrites in question differs essentially from the only two that chemistry as yet acknowledges. In either case all that can be concluded from the analysis is the presence of much iron, of a little sulphur, and of less nickel.

After examining the pyrites Mr. H. undertook the analysis of the metallic iron of the aerolite, which being treated in the way already described in the article IRON, appeared to be an alloy of about 17 parts iron and 6 nickel.

The globular concretions were then analysed by fusion with potash in the usual way and afforded

50	silex
15	magnesia
34	oxide of iron
2.5	oxide of nickel

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101.5

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Lastly, the earthy matter, which served as a cement for the three other ingredients, was examined in the same manner as the globular concretions were, and yielded

48	silex
18	magnesia
34	oxide of iron
2½	oxide of nickel

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102.5

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The excess in both these analyses is no doubt to be attributed to the difference of oxydation of the iron as existing in the substance and as obtained by analysis.

The component parts of the stones from Sienna, from Yorkshire, and from Bohemia, being in too small grains to allow of their separation with sufficient exactness, a small portion of each specimen was pulverized and examined in the usual way. They all afforded silex, magnesia, the oxides of iron and of nickel, and nothing else; thus exhibiting a perfect analogy with each other and with the aerolite from Benares.

It deserves to be remarked how striking a resemblance as to their component parts exists between the earthy parts of these aerolites, and the granular peridot or olivine which is almost peculiar to basalt; this substance being composed according to Klaproth of

50	silex
38	magnesia
12	oxide of iron

It is further worthy of notice that the external characters of the small transparent globule found in the stone from Sienna for the most part agree with those of the transparent globules that occur in the cells of the supposed meteoric iron from Siberia; and that these are also strikingly similar to those of olivine.

It remains to take some notice of a few other aerolites of still more recent origin, and which have exhibited certain peculiarities in their analysis.

8. On \* the 12th of March, 1798, the air being calm and without clouds, the inhabitants of Valence, in the Lyonnais, and its neighbourhood, were alarmed with the appearance of a meteor, accompanied by a singular noise, and exhibiting partial explosions. It was seen to fall in a vineyard, and on the day after, when the terror of the peasants had in a degree subsided, an officer of the police being present, search was made in the vineyard, a recent irregular hole of the depth of about 20 inches presented itself, at the bottom of which was found a black stone weighing above 20 lbs. On being broken it appeared to be composed of a granular ash-grey earthy matter, in which were imbedded grains of metallic iron, and of pale reddish yellow pyrites, with globular concretions of a grey colour, and some small irregular masses of a substance resembling olive coloured

\* Journ. de Phys. 1802.

steatite. A portion of the entire stone being analysed by Vauquelin afforded

- 46. silice
- 15. magnesia
- 2. lime
- 38. oxide of iron
- 2. oxide of nickel

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103.

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9. On the 26th of April,<sup>a</sup> 1803, about one o'clock in the afternoon, the air being calm and only a few clouds floating in the sky, a brilliant meteor was observed moving rapidly from S. to N. in the vicinity of the town of l'Aigle, in Normandy. In a few seconds afterwards there was heard at l'Aigle, and all around to the distance of even 90 miles radius, a violent explosion which lasted five or six minutes: this was succeeded by three or four bursts like the discharge of cannon, and by a number of smaller explosions like musket firing, the whole being terminated by a noise like the roll of a prodigious drum. These sounds evidently proceeded from a small cloud which appeared to be nearly stationary during the whole time, and the vapours of which it was composed were thrown out on all sides during each explosion. The inhabitants of the district immediately under the cloud were also alarmed by the hissing noise as of stones discharged from slings, and at the same time a multitude of masses of solid matter were observed to fall to the ground. The area upon which these stones fell is an irregular ellipse about 7 miles long by 3 miles wide; the largest stones were found at the S. Eastern extremity of this space, the smallest ones at the opposite extremity, while the middle-sized occupied the middle of the area. The size of the stones varied from 18lbs. to a quarter of an ounce: their number could not be ascertained, but they certainly amounted to some thousands. They were so hot when they fell as to burn those who attempted to take them up, their odour was sulphureous, or rather like that arising from the discharge of gunpowder. In their external characters, and as far as can be judged from a coarse analysis of them by M. Sage, they bear a close analogy to those which have been already described.

10. On the 15th of March, 1806,<sup>b</sup> a loud explosion with a roll like thunder was heard at Valence Dept. Du Gard, and immediately afterwards a stone weighing about 4 lbs. was observed to fall; in its descent it broke a

branch of a fig-tree and buried itself a few inches in the soil, (at the same time another stone of the weight of eight or nine lbs. was observed to fall in the adjacent district of St. Etienne). This aerolite differs greatly in appearance from all those that have been hitherto observed. It is black throughout its whole substance, and is composed of slightly adhering friable lamellæ; when rubbed on paper it leaves a grey trace not unlike that of plumbago: it acquires a kind of bituminous polish by friction, and by bruising in a mortar it is reduced to thin flat plates instead of powder. When heated it exhales a slightly bituminous odour. Its specific gravity is 1.94. Certain small granular portions of the stone were found to be attracted by the magnet. When calcined in contact with air its colour soon changed from black to red, without losing any weight; but when ignited in a small retort it remained black, gave out a little carbonic acid, and lost about 17 per cent. of its weight, which probably was water, which its porous structure enables it readily to absorb. By ebullition with muriatic acid it affords a very small quantity of sulphuretted hydrogen. It has been analysed by Vauquelin with the following result:

- 38. sub-oxide of iron
- 30. silice
- 14. magnesia
- 2. oxide of nickel
- 2. oxide of manganese
- 2. oxide of chrome
- 2.5 carbonaceous matter

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90.5

9.5 sulphur, water, and loss

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An analysis of the same substance has been published by Thenard, who found in it the same ingredients as those already mentioned, but in somewhat different proportions. Mr. Howard's analyses of the aerolites related above, were not calculated to detect the presence either of manganese or of chrome; as far therefore as certainly appears, the loose texture of this stone and the presence of a little carbonaceous matter are the principal circumstances in which it differs from the other meteoric stones. If at the period of its formation or explosion it had been subjected to a high degree of heat, the iron and other metals would have been deoxygenated at the expense of the carbon, and this would probably have also induced a greater compactness of structure, in which case

<sup>a</sup> Journ. de Phys. 1803.

<sup>b</sup> Ann. de Chim. lix. p. 34. 101.

the composition and probably the external characters would have been strictly analogous to those of the other aerolites.

11. On the 22d of May 1809,<sup>a</sup> an aerolite, or rather several, fell at Stannern in Moravia. Of the circumstances attending its fall there is no published account; the following are the external characters of a specimen in the possession of the Count d'Unin, and procured by him on the spot. Its external surface is black, and shows evident signs of fusion. Internally it presents a pale ash-grey earthy base in which are disseminated some concretions of a darker colour, and more compact than the rest of the mass; a few dispersed grains of pyrites are also visible. The entire stone is tender, friable, and its specific gravity is 3.19. It is not attracted by the magnet, but before the blow-pipe it fuses with difficulty into a black glass, which is then acted on by the magnet. On digestion in muriatic acid it affords a very small quantity of sulphuretted hydrogen. It has been analysed by Klaproth, by M. Moser of Vienna, and by Vauquelin. The particulars of Klaproth's analysis we are unacquainted with, being only informed in general that the composition of this aerolite bears a strong resemblance to that of basalt. Vauquelin's analysis, which was performed with much care, gives the following constituent parts of the entire stone.

- 50. silice
- 12. lime
- 9. alumine
- 29. oxide of iron
- 1. oxide of manganese
- nickel and sulphur, of each a trace.

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101.

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Hence it appears that the Moravian aerolite is specifically different from all those that have hitherto been described, by the absence of magnesia, and the presence of lime and of alumine.

12. The last meteoric stone<sup>b</sup> that we shall mention is one that fell near Sigena in Arragon, in the year 1773, and was deposited in the royal museum at Madrid. In 1805 M. Proust obtained leave to analyse a portion of it, and to publish the result, with a description of the stone. Its present weight is 6 lbs 10oz. but several fragments have been broken from it; where the surface is unbroken it presents the black vitreous crust which is characteristic of most of these bodies. Its colour internally is a light bluish grey. It is an aggregate of

globular concretions the largest of which are scarcely bigger than hemp-seeds, and which on examination with a lens are evidently covered over with extremely minute crystalline points. Intermixed irregularly with these concretions are particles of bronze coloured pyrites and of metallic matter. On pulverizing portions of the stone, and separating by the magnet the metallic particles, their proportion to the rest of the mass was found to vary from 17 to 22 per cent. This metallic matter was an alloy of iron and nickel in the proportion of 97 of the former to about 3. of the latter. The rest of the stone, including the pyrites, was then analysed and afforded by the usual methods,

- 12. sub-sulphuret of iron
- 5. black oxide of ditto
- 66. silice
- 20. magnesia

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103.

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The excess of weight in this as in the preceding cases is no doubt to be attributed to the oxidation of the iron.

#### AFFINITY.

M. Berthollet, one of the most profound and eminent chemical philosophers of the age, has endeavoured to shew that it is the tendency of chemical affinity to combine bodies in all proportions, so that where any limits to this indefinite combination appear, they arise from the operation of circumstances distinct from chemical affinity, which essentially modify its action.

On the other hand it is advanced by many most ingenious chemists, and supported by a daily increasing body of experiments, that substances unite in proportions which are rendered definite by the sole operation of their mutual affinity, and are equally definite whether only one or more compounds of the same bodies exist.

To this opinion, which has been advanced by Richter, Proust, and other eminent chemists, Mr. Dalton<sup>a</sup> has added a most important rule (supported by a variety of striking examples) which is, that where two bodies combine in different proportions, if the quantity of one of them be assumed as a fixed number, the proportions of the other body that unite to it are in the simplest possible ratio to each other, being produced by multiplying the lowest proportion by a simple integral number as 2, 3, 4, &c.

Thus for example, if a metal can combine

<sup>a</sup> Ann. de Chim. lxx. 321.

<sup>b</sup> Journ. de Phys. 1805.

<sup>c</sup> New System of Chemical Philosophy.

chemically with different proportions of oxygen, if 100 of the metal take 9 of oxygen for the lowest degree of oxygenation, all the other degrees will be in the proportion of 100 of metal to twice 9 (18) of oxygen; or 100 of metal to three times 9 (27) of oxygen; or 100 of metal to four times 9 (36) of oxygen, &c. &c. A reason for this simplicity in the ratio of binary compounds may be found in the general principle assumed by Mr. Dalton, which is, that in all cases the simple elements of bodies are disposed to unite atom to atom singly, or if either is in excess it exceeds by a ratio to be expressed by some simple multiple of the number of its atoms.

Hence, from the relative weights of the constituent parts of a compound, Mr. Dalton infers the relative weights of the ultimate particle or atom of each of these parts; and, this being found, the number of atoms of each constituent which enters into the formation of the compound particle is also deduced.

Thus (taking a compound of two constituent parts A and B. as the simplest case) if its elements are found by experiment to unite in the proportion of 5 of A to 7 of B, it is inferred by Mr. Dalton that the numbers 5 and 7 express the comparative weight of an atom of A and B. respectively. And these elements, though uniting in several proportions, will yet be found by experiment to be confined to either 5 A to 14, 21, 28, &c. of B, which is, one atom of A to 2, 3, 4, &c. atoms of B; or conversely it will be 7 B to 10, 15, 20, &c. of A, which is one atom of B, to 2, 3, 4, &c. atoms of A. It is essential to the consistency of this system therefore, that there should be no other proportions of combination between these two elements, unless indeed it be one that is expressed by an even sub-division of one of these proportions, as for example, 5 A to 7,  $10\frac{1}{2}$ , 14, &c. of B; in which case the  $10\frac{1}{2}$  being resolvable into three portions of  $3\frac{1}{2}$  each, the number expressing the relative weight of an atom of B, must be reduced to  $3\frac{1}{2}$  instead of 7, and consequently the several proportions of 7,  $10\frac{1}{2}$ , 14, and 21 of B, will be resolved respectively into 2, 3, 4, and 6 atoms of B.

To verify the numbers expressing the relative weights of an atom of A and B, (supposing that of A to be assumed as 5, and that of B as 7) let them each be examined in their separate compounds with a third body, C. Then, suppose that in the simplest binary compound of A and C, analysis discovers 3 parts by weight of C, to 5 of A, it is assumed, that, as 5 is

taken as the numerical expression of an atom of A, the number expressing an atom of C, must be 3; and *consequently*, if this mode of estimation be just, it will also be found by experiment that in the simplest combination of C with B, 7 parts of B will unite exactly with 3 parts of C. This supposes indeed that this simple combination of one atom of each body is known by experiment; but even if this should not be the case, the general principle will not be contravened, if, instead of a single portion of C being found, there should be a double, triple, or quadruple portion, provided the radical number or common divisor is 3, that of B being 7.

To illustrate this by an example from Mr. Dalton (in which however the numbers assumed are not perfectly accurate though sufficient for the present purpose.) The substance of which as far as we yet know the smallest relative weight enters into chemical combination is hydrogen, and on this account the weight of its atom is assumed as unity, and is the standard of comparison for the relative weight of the atom of all other bodies. The only compound of hydrogen and oxygen that we know is water, in which the oxygen is to the hydrogen as 7 to 1. The number 7 therefore is assumed as the relative weight of the atom of oxygen, and water is a binary compound containing an atom of hydrogen with an atom of oxygen in every atom of water. Sulphuretted hydrogen is composed according to Mr. Dalton of 13 parts by weight of sulphur and 1 of hydrogen. If it be assumed that an atom of sulphuretted hydrogen contains an atom of sulphur united to an atom of hydrogen, the relative weight of an atom of sulphur must be 13. To prove that this number 13 may be assumed as the weight of an atom of sulphur, let it be examined in its compounds with oxygen, and if correct, all the compounds of these two elements will contain for every 13 parts by weight of sulphur, either 7, or 14, or 21, &c. parts of oxygen, according as the compound contains to every atom of sulphur one, or two, or three atoms of oxygen.

Now according to Mr. Dalton *Sulphureous acid* actually contains 13 parts by weight of sulphur to 14 of oxygen, and therefore its atom consists of one atom of sulphur to two atoms of oxygen; and *Sulphuric acid* consists of 13 parts by weight of sulphur to 21 of oxygen, or one atom of the former to three atoms of the latter.

This hypothesis therefore is perfectly consistent in the above examples.



The comparative *weight* of each atom being thus ascertained, the relative *diameter* of the atom is found by comparing its relative weight with the specific gravity of the substance of which the atom is an integrant particle. But as this part of Mr. Dalton's system is not essential to our present purpose we shall not pursue it.

Not only do elementary atoms unite in definite proportions but also compound particles unite in the same manner. Thus both sulphuric acid and potash are compound particles, being each oxyds, the one of sulphur and the other of potassium. But as potash combines with two different proportions of sulphuric acid, one being just double the quantity of the other, the compound, *sulphat of potash*, may with propriety be considered as composed of an atom of potash with an atom of sulphuric acid, and the compound, *super-sulphat of potash*, may be considered as consisting of one atom of potash to two atoms of sulphuric acid.

Mr. Dalton gives the term *Binary atom* to any compound of two elements in which one atom of each is combined, and hence there can be but one species of binary compound of any two elements.

A *Ternary Atom* is composed of two atoms of one of the elements with one atom of the other, and hence there may be two species of ternary atoms of the same element, according as one or other is in the greater proportion. Thus an atom of nitrous oxyd is a ternary compound of two atoms of azote and one atom of oxygen; and on the other hand nitrous acid is also a ternary compound of the same elements, but consisting of one atom of azote with two atoms of oxygen.

A *Quaternary Atom* is composed of three atoms of one element with one atom of the other, and hence also there may be two species of quaternary atoms as either element predominates; and so on of the other numbers.

We shall now proceed to mention a number of facts that illustrate in a striking manner the chemical union of substances in *definite proportions*.

If one measure of pure oxygen and two measures of hydrogen be mixed in a jar over mercury and ignited by the electric spark, both the gasses will disappear, and water will be produced. If two measures of each gas be used, water will be produced as before, but one measure of oxygen will remain. Hydrogen there-

fore unites with water in one exact proportion, and in no other.

If a piece of well burnt charcoal be confined in oxygen gas and inflamed by a burning glass the volume of gas is not altered when again cooled, but the whole is converted into carbonic acid gas. If more oxygen be present than is necessary for the consumption of the charcoal, the products will be carbonic acid gas and an excess of oxygen; if there is less oxygen than will consume the charcoal, carbonic acid alone will be produced, and part of the charcoal will remain unconsumed.

The combination of two elements in several definite proportions is very happily shewn by the various compounds of oxygen and azote. These are nitrous oxyd, nitrous gas, and nitrous acid gas.

If two measures of *Nitrous Oxyd*, and two measures of hydrogen are ignited by the electric spark, the product is water, and two measures of azote remain. Now as water is produced by two measures of hydrogen and one of oxygen the nitrous oxyd here employed must have consisted of two measures of azote with one of oxygen condensed into the space of one measure.

If charcoal is ignited in two measures of *Nitrous gas* the products are one measure of carbonic acid gas and one measure of azote. Hence, as carbonic acid gas always occupies the same volume as the oxygen of which it is formed, nitrous gas consists of equal volumes of oxygen and of azote not condensed by their union.

If two measures of nitrous gas be mixed over water with one measure of oxygen gas, both of them totally disappear, and a solution of *Nitrous acid gas* in water is the result.

In all the above examples the proportions of azote and oxygen increase or diminish by equal quantities, and no intermediate states of combination are known.

Dr. Wollaston has given some striking experiments in illustration of this theory of definite proportions in the composition of some super-acid and sub-acid salts,<sup>b</sup> which may be here mentioned as they are easily performed. Let two grains of crystallized carbonat of potash recently prepared be wrapped in thin paper, and passed up into an inverted tube filled with mercury, and let the gas be extricated from it by muriatic acid, and the space it occupies be marked on the tube. Then let four grains of the same carbonat be exposed for a short time to

<sup>b</sup> Phil. Trans. for 1808.

a red-heat, and afterwards let the gas be expelled from it in the same apparatus, and it will be found to occupy exactly the same space as that obtained from the two grains of crystallized salt in the former experiment.

The same results are obtained from the super-carbonat and the sub-carbonat of soda.

Super-sulphat of potash in like manner contains twice the quantity of acid as the neutral sulphat. Let twenty grains of carbonat of potash be mixed with about twenty-five grains of sulphuric acid in a covered platina crucible, or in a glass tube, and this mixture gradually heated till it ceases to boil and becomes slightly red-hot. This will produce the super-sulphat of potash, which will be very nearly neutralized by an addition of 20 grains of the same carbonat of potash.

The common super-oxalat of potash is shewn by Dr. Thomson to consist of potash united to twice the quantity of oxalic acid necessary to saturate it. If two equal portions of this super-oxalat be taken, and one portion calcined so as to destroy the acid, the alkali that remains will be just sufficient to saturate the other portion.

When nitric or muriatic acid is added to the common super-oxalat of potash, the latter salt is only partially decomposed, and crystals form in the mixture which are found on examination to be a *Quadroxalat of Potash*, or potash with four times as much acid as will saturate it.

The formation of these various salts with a definite excess of acid which is expressed by a simple multiple of the least definite quantity is particularly important as it affords an answer to the powerful objection urged by M. Berthollet against the common opinion of chemical affinity. This eminent chemist shews that a considerable excess of a weaker acid will decompose a compound of a base and a stronger acid; for example, that a large quantity of nitric acid added to sulphat of potash will occasion some crystals of nitre to form, though the nitric acid has a weaker affinity to potash than the sulphuric. But though there is an undoubted decomposition of some portion of the sulphat of

potash in this case, it is highly probable that for every particle of nitre formed there is an equivalent quantity of a super-sulphat of potash produced, in equally definite proportions with the neutral sulphat, and in which probably the acid is in the ratio of a simple multiple of that which exists in the neutral salt.

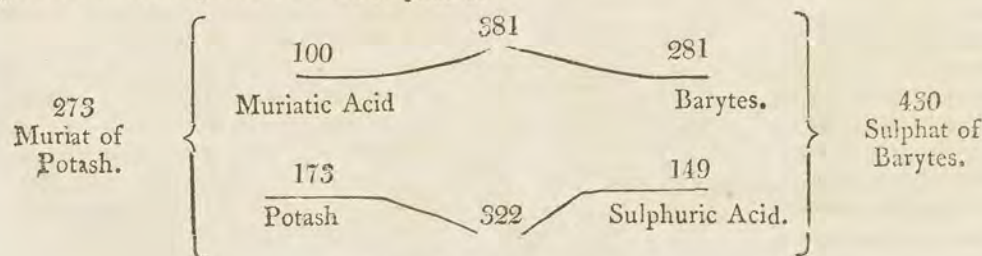
Among the philosophers who within these last few years have laboured with the greatest zeal and success in discovering the laws of chemical affinity a distinguished place is due to Professor Berzelius,\* whose experiments we shall now briefly notice. He states that he was led to this train of enquiry from the two following most important theorems laid down by the learned Richter.

1. When two bodies A. and B. have each an affinity for two others C. and D. the C. which saturates a given quantity of A. is to the D. which saturates the same quantity of A. in the same proportion as the C. saturating any given quantity of B. is to the D. saturating the same quantity of B. Hence the saturating proportions of A. C. A. D. and B. C. being known those of B. D. may be found by simple calculation. For example, let A. B. C. and D. be respectively sulphuric acid, muriatic acid, barytes and potash, and let 100 parts of sulphuric acid be saturated by 190 of barytes, and by 116 of potash, and let 100 of muriatic acid be saturated by 281 of barytes, then, the quantity of potash saturating 100 of muriatic acid will be 173;

Bar. Pot. Bar. Pot.

for 190 : 116 :: 281 : 173 nearly.

This law of chemical combination is indeed a direct inference from the fact that when two neutral salts are mixed together and decompose each other the mixture remains neutral. Thus, supposing 381 parts of muriat of barytes be exactly decomposed by 322 parts of sulphat of potash, and the mixture remain neutral, the respective proportions of the new compounds formed will be 273 of muriat of potash, and 430 of sulphat of barytes, as by the following scheme :



\* An. Chim. Tom. 77 to 83 inclusive.

The *respective* proportions of potash and barytes that saturate any acid are always as 173:281, and in the decomposition here assumed the muriatic acid that saturates these bases is 100 parts. Therefore the sulphuric acid must be 149 parts as calculated both from the elements of sulphat of potash and sulphat of barytes. In the former case 116 of potash saturate 100 parts of sulphuric acid, and 116 : 100 :: 173 : 149. In the latter case 190 of barytes saturate 100 of sulphuric acid, and 190 : 100 :: 281 : 149.

The importance of this law of chemical combination is so great that the composition of all the binary compounds might be found with absolute certainty, provided the data founded on actual experiment could be brought to perfect accuracy. Hitherto however this has not been the case, as no series of numbers representing the neutral compounds has yet been given which will apply throughout. It is a chief part of the present labours of Prof. Berzelius to correct the elements of these calculations by varied experiments conducted with great care and intelligence.

Another equally important law laid down by Richter is, that when the metal of a neutral metallic solution is precipitated by another metal, it is the metallic base alone which is changed, the oxygen and the acid remaining united with the last added metal. Hence it follows that all the different metallic oxyds which saturate a definite portion of acid contain the same quantity of oxygen. Or in other words it may be expressed that a given quantity of any acid combines to saturation with only a definite proportion of oxygen united to so much of any base as contains this portion of oxygen. Thus for example, if 100 parts of sulphuric acid saturate 20 parts of oxygen and the base united with it, the proportion of every oxyd that combines with 100 of sulphuric acid, and the composition of every neutral sulphat is known as soon as the oxyd itself is analyzed. And, conversely, the composition of any unknown oxyd may be discovered by finding the quantity of this oxyd which neutralizes a given weight of any acid whose saturating quantity of oxygen in any other oxyd is previously known. Thus, for example, if 100 parts of sulphuric acid saturate any oxyd that contains 20. of oxygen, it may be inferred that 116 parts of potash are composed of 20 of oxygen and 96 of potassium, since this quantity of potash saturates 100 of sulphuric acid. The like quantity of oxygen is therefore contained in 78 of soda, in 190 of

barytes, &c. &c. each of which saturate 100 of sulphuric acid.

The late discovery of the compound nature of the alkalies and earths therefore gives an additional importance to this law of chemical affinity.

Another law of chemical combination which is laid down by Berzelius, and illustrated by numerous examples, is the following, viz. In any compound of two oxydated substances, that substance which is attracted to the positive pole of the electric circuit (the acid, for example) contains as much oxygen as is produced by multiplying the oxygen of the substance attracted to the negative pole (such as alkali, earth, metallic oxyd) by some of the integral numbers 2, 3, 4, 5, &c. For example, as 100 parts of sulphuric acid saturate as much of any oxyd as contains about 20 parts of oxygen, the quantity of oxygen in 100 parts of the acid itself must be equal to twice 20, or three times 20, &c. In this example it will be shewn presently that sulphuric acid contains almost exactly three times 20, or 60, per cent. of oxygen. Most of the other acids however contain only twice the oxygen of their saturating base: the carbonic and sulphureous acids are of this kind.

In all the compounds in which water forms an element (which are all the crystallized salts and liquid acids) this substance also seems to be subjected to some similar law of definite proportion, as will be soon explained.

We shall now give a short abstract of a few of the important series of Prof. Berzelius' experiments, to shew to what degree they illustrate and confirm the above laws of chemical combination, together with some others which will be stated in their place.

The composition of sulphuric acid which has so often been attempted was ascertained in several methods; and first through the medium of the oxyd and sulphuret of lead.

*Lead and Oxygen.* Lead has three degrees of oxygenation, viz. the yellow, the red, and the brown.

For the yellow oxyd, some pure lead (reduced from the nitrat of lead) was dissolved in nitric acid evaporated and ignited; a hundred parts of metal thus gained 7.8 of oxygen.

The red oxyd, or purified minium, contains to 100. of metal 11.07 oxygen.

The brown oxyd formed by digesting minium in nitric acid, contains to 100. of metal 15.6 of oxygen.

Therefore these portions of oxygen, viz. 7.8;

11.07; and 15.6, are respectively in the proportions of 1,  $1\frac{1}{2}$  and 2.

The yellow oxyd is the only one which enters into the salts of lead.

*Lead and Sulphur.* 100 parts of lead mixed with as much pure sulphur, and heated in a close vessel, as long as any sulphur was sublimed, produced 115.6 of the sulphuret; so that 100 parts of lead when thus united with sulphur absorb 15.6, which is exactly twice the weight of oxygen united with the same quantity of lead in the yellow oxyd. On this coincidence a law of combination is deduced which will be presently mentioned.

This sulphuret of lead is therefore thus composed:

	Oxygen.	
Lead - 86.51	with 6.748	produce 93.258 oxyd of lead
Sulphur 13.49	— 19.752	— 33.242 sulphuric acid
Sulphuret of lead 100.00	26.500	126.5 sulphat of lead

Two things are to be particularly noticed here:

One of them is: that the sulphur of the sulphuret of lead was exactly sufficient when converted to sulphuric acid to saturate the lead of the same sulphuret when converted to the suboxyd of lead.

The other thing to be noticed is: that the quantity of the sulphur in the sulphuret was almost exactly double the quantity of oxygen taken up by the lead of the sulphuret, being as 13.49 to 6.748.

From the former of these facts the author infers as a general rule, that a metal combines with sulphur in such a proportion, that when the sulphur is converted to sulphuric acid and the metal to an oxyd, the sole product will be a neutral sulphated oxyd of the same metal.

From the latter of these two facts the author infers: that in every neutral sulphat the oxygen of the base equals half the weight of the sulphur of the acid with which it is saturated.

The composition of sulphuric acid is inferred from the above oxydation of sulphuret of lead, to be in the proportion of 13.49 of sulphur to 19.752 of oxygen, the whole addition of oxygen to the sulphuret being 26.5, and 6.748 of this being estimated as the portion belonging to the oxyd of lead.

Sulphuric acid therefore consists of		
Sulphur 40.58	—	100.000
Oxygen 59.42	—	146.426
100.00		246.426

Lead . 100		86.51
Sulphur 15.6		13.49
115.6		100.00

A hundred parts of the sulphuret of lead last described were digested in nitro-muriatic acid till the whole was converted into sulphat of lead, the sulphur and lead both acquiring oxygen from the nitro-muriatic acid. No product whatever was yielded from the sulphuret but the sulphat of lead, which was perfectly neutral and weighed 126.5 parts. The respective changes that took place therefore, supposing the base of this salt to be the yellow oxyd, are as follows:

According to the second of the two propositions just mentioned, 100 parts of sulphuric acid therefore will saturate so much of any oxydated base as contains  $\frac{40.58}{2} = 20.29$  of oxygen.

As an exact determination of the elements of sulphuric acid is of great importance in analysis, the author proceeds to compare the above mentioned result with those produced by other modes of operating.

Both Bucholz and Klaproth have sought to fix the elements of this acid by acidifying a given quantity of sulphur, and then combining it with the barytes of a known quantity of some soluble barytic salt. The analysis of sulphat of barytes depends also on that of carbonat of barytes, out of which all the barytic salts are prepared. By multiplied experiments the author fixes the elements of carbonat of barytes at

Carbonic acid 21.6	—	100
Barytes 78.4	—	363
100.0		463

Of this carbonat, 100 parts (containing 78.4 of base) gave from 118.6 to 119 parts of sulphat of barytes, which will give for the elements of sulphat of barytes within  $\frac{1}{10000}$  of the following numbers:

Sulphuric acid 34	—	100
Barytes 66	—	194
100		294

Bucholz acidified 100 parts of fused sulphur with nitro-muriatic acid, and by combining with barytes the sulphuric acid thus produced obtained 724 parts of sulphat of barytes. If this sulphat is estimated according to Berzelius' result above given, its acid part will be 246.16, whence 100 parts of sulphur will have combined with 146.16 of oxygen, and this estimation of sulphuric acid will be found to correspond almost exactly with that already given as found by the acidification of sulphuret of lead.

*Sulphureous Acid.* The production of this acid by the direct combustion of sulphur being attended with nearly insuperable difficulties, Pr. Berzelius attempted its analysis by means of the sulphite of ammonia. This salt was decomposed by muriat of barytes, and the resulting sulphite of barytes was changed to the sulphat of barytes, by means of nitric acid, none of the sulphureous acid being expelled in the process. By these and other experiments the author determines the elements of sulphureous acid to be

Sulphur	50.57	—	100.00
Oxygen	49.43	—	97.83
	<u>100.00</u>		<u>197.83</u>

The oxygen in the sulphureous acid is therefore to that in the sulphuric acid very nearly as  $1:1\frac{1}{2}$ ; as 100 parts of sulphur unite with 97.83 of oxygen in the sulphureous, and with 146.426 in the sulphuric, and  $79.83 \times 1\frac{1}{2} = 119.7425$ .

*Copper with Sulphur and Oxygen.*

The author proceeds to examine the com-

Copper	100.0	with 12.800 oxygen give	112.800 suboxyd of copper
Sulphur	25.6		63.085 sulphuric acid
	<u>125.6</u>		<u>175.885 Sulphated Suboxyd of Copper</u>

This therefore would give for the composition of the suboxyd of copper,

Copper	100.0	—	88.652
Oxygen	12.8	—	11.348
	<u>112.8</u>		<u>100.000</u>

And the sulphated suboxyd of copper would consist of 63.085 acid to 112.8 of suboxyd: or as follows: (the oxygen of the base equalling half the sulphur in the acid).

Sulphuric acid	100.0	—	35.87
Suboxyd of copper	178.8	—	64.13
	<u>278.8</u>		<u>100.00</u>

pounds of copper with sulphur and oxygen, to ascertain whether they agree with those of lead in the three laws of combination which he had laid down. These laws (to repeat them) are the following:

1. That the sulphuret of any metal, when oxydated, is totally changed to a neutral sulphat.
2. That in every sulphat the oxygen belonging to the base equals half the weight of the sulphur in the acid.
3. That in every compound of an acid and a base, the oxygen of the acid equals that of the base multiplied by some integral number. To this may be added the other law of all chemical combination (which is entirely adopted by the author) namely,
4. That where two bodies unite in different proportions, if the quantity of one of them be assumed as a fixed number, the proportions of the other body are in the simplest ratio to each other, being produced by multiplying the lowest proportion by some integral number.

*Copper and Sulphur.* One hundred parts of copper heated in a retort with as much sulphur, till all the excess of the latter was expelled, produced 125.6 of sulphuret of copper. Some difficulties attend this operation to produce uniform results, but the above number appears to approach the nearest to accuracy. Hence from this single fact, the following composition of the suboxyd and sulphated suboxyd of copper should be made out, assuming that the oxyd of copper corresponding with this sulphuret is at a minimum of oxydation.

Now, supposing the *Peroxyd* of copper to contain twice the quantity of oxygen to a given weight of metal, as the suboxyd, this peroxyd of copper would consist of

Copper	100.0	—	79.618
Oxygen	25.6	—	20.382
	<u>125.6</u>		<u>100.000</u>

Then if this peroxyd were the base of a neutral sulphat of copper, this sulphated peroxyd would contain

Sulphuric acid	100.000	—	50.113
Peroxyd of Copper	99.548	—	49.887
	<u>199.548</u>		<u>100.000</u>

since 99.548 would be the quantity of this peroxyd that contains oxygen equal to half the sulphur in the acid.

Lastly, if this latter sulphat were formed by

Copper	-	100.0	Oxygen.	with	25.60	give	125.60	peroxyd of copper
Sulphur	-	51.2			74.97		126.17	sulphuric acid
Super-sulphuret		<u>151.2</u>			<u>100.57</u>		<u>251.77</u>	Sulphated Peroxyd of Copper

The author then proceeds to examine the accuracy of these hypothetical numbers by actual experiment. We shall state them in a very few words.

The peroxyd of copper was formed by evaporating and igniting a given weight of metal dissolved in nitric acid. Another portion of the nitrat was decomposed by a carbonated alkali, and the precipitate ignited. In the former case some of the metal was volatilized with the acid, and in the latter a portion was left in the solution and separated by sulphuretted hydrogen, both of which circumstances produce some little inaccuracy in the results. An allowance must also be made for the sulphur and carbon retained by all copper. If this be fixed at  $\frac{1}{2}$  per cent. (which however is quite arbitrary) the composition of the peroxyd of copper will be

Copper	80	—	100
Oxygen	20	—	25
	<u>100</u>		<u>125</u>

which very nearly agrees with the proportion deduced from the sulphuret.

The suboxyd of copper was formed by mixing 10 parts of the peroxyd with the same quantity of pure copper in a flask, containing 75 parts of muriatic acid, and keeping the vessel well closed on a gentle stove-heat for three days, with frequent shaking. After this the whole of the peroxyd and part of the copper were dissolved, and the quantity of the latter was found by weighing the undissolved portion. Then supposing the oxygen of the peroxyd to be equally divided between its own portion of metal and that added, and the whole to constitute the suboxyd, this will nearly contain half the oxygen of that in the peroxyd, allowing a small deviation to be produced by the unavoidable action of the muriatic acid on a small portion of the copper, independently of the oxygen present, which was shewn by an escape of hydrogen when the vessel was opened. A suboxyd of copper containing half the oxygen of the peroxyd, will therefore consist of

the direct oxygenation of a super-sulphuret of copper, this would of course contain a double proportion of sulphur, and its proportions when resolved would be as follows :

Copper	88.89	—	100.0
Oxygen	11.11	—	12.5
	<u>100.00</u>		<u>112.5</u>

This very nearly agrees with the result of a similar experiment made by Mr. Chenevix, who reckons 13. of oxygen to 100. of metal; and the composition of this suboxyd estimated from the sulphuret is the mean of these two, or 12.8 of oxygen.

The common sulphat of copper was then analyzed: 5 parts of this salt dried at a tin-melting heat and decomposed by muriat of barytes, gave 7.22 of sulphat of barytes, the acid of which is 2.455, leaving therefore 2.545 for the oxyd of copper in the 5 parts. The basis of this salt is the *peroxyd* of copper, and therefore this salt is properly the sulphated peroxyd of copper. It is thus composed, from the above analysis :

Sulphuric acid	49.10	100.00
Peroxyd of copper	50.90	103.66
	<u>100.00</u>	<u>203.66</u>

On the other hand, if 100 parts of sulphuric acid neutralize so much of any base as contains 20.29 parts of oxygen, it would require 101.45 instead of 103.66 of the peroxyd.

The quantity of peroxyd saturating 100. of sulphuric acid, as estimated by the composition of the sulphuret, is 99.548, which is still sufficiently near 103.66 to come within the limits of probable error.

The above experiments on the compounds of copper with sulphur and oxygen are so far defective that they do not exhibit any super-sulphuret of copper, which is the regular base of the common sulphat of copper or sulphated peroxyd: nor on the other hand do they shew any sulphated suboxyd of copper, which is the regular product of the oxydation of the subsulphuret actually known. They sufficiently illustrate, however, the law of definite proportions in the different degrees of oxydation; and that

of a precise portion of oxygen in the oxyd saturated by a given quantity of sulphuric acid.

*Iron, Sulphur and Oxygen.*

We shall briefly mention these, on account of an apparent anomaly in the relation between the sulphuret and sulphat as already laid down.

*Subsulphuret of Iron.* This was formed by heating red-hot for a considerable time a mixture of thin iron plate and thrice its weight of sulphur, till all the excess of the latter was sublimed. The remaining sulphuret of iron was brilliant, brittle, and magnetic only in powder. A given portion of it was analyzed by being first totally dissolved and acidified in nitro-muriatic acid, and the sulphuric acid thus generated was separated by muriat of barytes and the oxyd of iron by ammonia. Reckoning 34 per cent. of acid, or 13.797 of sulphur, in sulphat of barytes, and 69.3 per cent. of iron in the peroxyd here produced by the action of the nitro-muriatic acid, this subsulphuret of iron would consist nearly of

Sulphur . . . 37	—	58.75
Metallic iron . . . 63	—	100.00
		100
		158.75

The super-sulphuret of iron, or natural crystallized pyrites, gave by a similar analysis,

Sulphur . . . 53.92	—	117
Iron . . . 46.08	—	100
		100.00
		217

Therefore the sulphur combined with 100 parts of iron is twice as much in the super-sulphuret as in the subsulphuret.

*Oxyds of Iron.* This very important subject has been examined here with peculiar care. It was first asserted by Proust, and has been pretty generally allowed, that there are but two oxyds of iron, the black and the red oxyd, the former being the suboxyd and the latter the peroxyd. That there are these two distinct oxyds is not doubted, but Thenard has given some experiments which appear to establish

another oxyd of a still lower degree of oxygenation than the black oxyd, and which when first separated from its solution is *white*. If this be correct, there are three oxyds, namely, the white, the black, and the red, of which the latter has the highest proportion of oxygen. The existence of this white oxyd is also probable on account of the ratio of oxygenation, as will be further mentioned here, and also in the article *Iron* in this Appendix.

At present however only the black and the red oxyd are concerned, which may be here termed the Suboxyd and the Peroxyd.

The composition of these as determined by Berzelius from many experiments, is the following.

For the suboxyd		
Iron . . . 77.22	—	100.0
Oxygen . . . 22.78		29.5
		100.00
		129.5
For the peroxyd		
Iron . . . 69.34	—	100.00
Oxygen . . . 30.66		44.25
		100.00
		144.25

Therefore the oxygen of the peroxyd is to that of the suboxyd only as  $1\frac{1}{2}$ . to 1. for  $29.5 \times 1\frac{1}{2} = 44.25$ .

But on the other hand the sulphur of the super-sulphuret is twice the proportion of that in the sub-sulphuret: and therefore if each of these sulphurets were acidified and converted into a sulphat of iron (the base of the sulphat corresponding with the sub-sulphuret being the suboxyd, and that of the other sulphat being the peroxyd) it is evident that the laws that regulate this change as deduced from the sulphuret and sulphat of lead could not be preserved.

The combinations that would take place are as follows.

The sub-sulphuret converted into a sulphated suboxyd would give

Iron . . . 100.00	with	Oxygen.	29.50	.	give	129.5	Suboxyd
Sulphur . . . 58.75	—	86.03			—	144.78	Sulphuric acid
		158.75				274.28	Sulphated Suboxyd
		115.53					

In this case all the laws of combination are observed pretty accurately, the sulphuric acid saturating so much of the base as contains oxygen equal to half the sulphur in the acid,

within a trifling difference. But on the other hand, if the supersulphuret of iron or the natural crystallized pyrites (which contains a double proportion of sulphur) were totally

oxydated in the same way, and converted into a sulphat with the peroxyd for its base, it is obvious that the same relative proportions between the sulphat and the sulphuret could not be preserved, as the peroxyd is an oxygenation

of only  $1\frac{1}{2}$  the quantity of the suboxyd, whereas the supersulphuret is a sulphuration of twice the quantity in the subsulphuret. This compound therefore, if it could exist, must be one with a double portion of acid as follows :

	Oxygen.				
Iron . . .	100.00	with	42.25	.	give 144.25 Peroxyd
Sulphur . .	117.50	—	172.06	.	— 289.56 Sulphuric acid
Supersulphuret	217.50		214.31		433.81 Supersulphat

The resulting salt in this case therefore must be with excess of acid, for 289.56 : 144.25 :: 100 : 49.82 so that 100. of sulphuric acid would only unite with 49.82 of the peroxyd of iron which contains only 15.27 of oxygen ; whereas it is found by all the previous experiments that 100. of sulphuric acid requires for its saturation

as much of any oxyd as contains 20.29 of oxygen, or thereabouts.

But the actual composition of the sulphated peroxyd of iron (or *red sulphat*) is very different. Berzelius finds it by experiment to contain about 100 sulphuric acid to 65.5 peroxyd, which are resolved into the following numbers.

	Oxygen.				
Sulphuric acid 100	contain	59.42	with	40.58	Sulphur
Peroxyd . . .	65.5	—	20.10	—	45.40 Iron

These numbers agree sufficiently well with the laws of combination all along observed, for the oxygen of the peroxyd is very nearly half the weight of the sulphur in the acid, and 100 parts of the acid saturate as much peroxyd as contains 20.1 of oxygen. Therefore the sulphuret of iron, which is the base of this sulphat, is one in which the sulphur is to the iron as 40.58 : 45.40 and would therefore consist of

Iron	100.
Sulphur	89.38
189.38	

which is an intermediate degree of sulphuration between the two actually ascertained by experiment. A sulphuret not far deviating from these proportions has been actually produced by Mr. Hatchett by distilling the magnetical pyrites with sulphur in a low red heat, as mentioned in our original article IRON.<sup>a</sup>

#### Muriatic Acid.

A perfect analysis of muriat of silver that could be depended on even to a thousandth part is a great desideratum, as it would afford a means of ascertaining the muriatic acid in all the other muriats, and also the quantity of oxygen contained in the base of all these salts, if the hypothesis of equal saturation of acids by so much of every oxyd as contains a given portion of oxygen be correct. There is no great difficulty in ascertaining the quantity of metallic silver in a given portion of the fused muriat of silver, but it is not so easy to find the

exact proportion of oxygen that unites to the metal and of muriatic acid. It is thus attempted by Professor Berzelius.

*Muriat of Silver.* 100 of ignited carbonat of barytes contain by experiment 21.6 of carbonic acid, and therefore 78.4 of barytes, which last when saturated with muriatic acid gives 105.6 of muriat of barytes, which salt therefore contains 78.4 of barytes, and 27.2 of acid. Hence the elements of muriat of barytes are

Muriatic acid	25.75	100.0
Barytes . . .	74.25	288.4
100.00		388.4

On the other hand 105.6 of muriat of barytes decomposed by nitrat of silver produce 145.5 of fused muriat of silver, which last therefore contains all the acid in 105.6 muriat of barytes, namely, 27.2 parts, and 144.5 : 272 :: 100 : 18.7. Therefore 100. parts of muriat of silver contain 18.7 acid and 81.3 oxyd of silver.

Likewise, 100 parts of silver being dissolved in nitric acid, muriatic acid added in excess, and the whole evaporated and fused gave 132.7 of muriat of silver, the metal of which therefore is 100. parts, or (reduced to the proportion of 100 parts of the muriat of silver) this will contain 75.358 per cent. of silver, and 24.642 oxygen and muriatic acid.

But as muriat of silver has already been shewn to contain 18.7 per cent. of muriatic acid, the difference between 24.644 and 18.7, or 5.942, is the oxygen.

<sup>a</sup> See Chem. Dict. vol. 1.



From these data therefore the fused muriat of silver is thus composed :

Muriatic acid . . . . .	18.7 . . . . .		Silver . . . . .	402.984 } . . . . .	100.000
Silver . . . . .	75.358 } . . . . .	81.3	Oxygen . . . . .	31.775 } . . . . .	434.759
Oxygen . . . . .	5.942 } . . . . .				
	100.0			534.759	

And the oxyd of silver will consist of

silver . . . . .	92.67 . . . . .		oxygen . . . . .	7.925 . . . . .	100.000
	100.00			107.925	

Therefore 100 parts of muriatic acid saturate so much of this base as contains 31.775 of oxygen, and if the rule of equal saturation be just, every base that saturates 100. parts of dry muriatic acid will contain 31.775 of oxygen, provided this analysis of muriat of silver be correct.

Another mode of analysing muriat of silver is by means of the sulphuret. Sulphuret of silver the author finds to consist of 100 silver to 14.9 sulphur; sulphuret of lead contains 100 lead and 15.42 sulphur; and suboxyd of lead contains 100 of lead to 7.7 oxygen. Then, applying Richter's rule, the sulphur saturating 100 parts of lead, is to the oxygen saturating 100 of lead, in the same proportion as the sulphur saturating 100 of silver is to the oxygen saturating 100 of silver. This will give 7.44 for the oxygen saturating 100 of silver; for 15.42 : 7.7 :: 14.9 : 7.44. If this result be taken in conjunction with the fact that 100. of silver produce 132.7 of the muriat of silver, this 132.7 of muriat will consist of 100. of silver, and 7.44 of oxygen, leaving 25.26 for the muriatic acid. This would give as much as 19.035 per cent. of muriatic acid in muriat of silver, and only 6.925 per cent. of oxygen in the oxyd of silver; and would give only 29.455 for the oxygen in the base saturated by 100. of dry muriatic acid.

As the latter mode of estimating muriat of silver is obviously exposed to many more sources of inaccuracy, the former is preferable. All things considered, the disagreement between the two is not very great, though sufficient to render it unsafe to take the mean number as the most accurate. We may therefore for the present infer that a dry saturated muriat (retaining the old theory of muriatic acid) contains for every 100 parts of muriatic acid about 31.5 of oxygen in the base which saturates the acid.

The author examines the muriats of copper

and lead with this view. The particulars we shall not here give, but the results considerably confirm this general law of equal saturation above mentioned.

*On Water of Crystallization and Water of Composition.*

Water according to Berzelius performs the part of a base when united to an acid, and of an acid when in union with a base. Some acids cannot exist in a separate state unless combined with a certain portion of water, which portion is exactly sufficient to oxydate that quantity of any metal which will combine with the acid to form a neutral compound. This is the case most remarkably with the muriatic acid, and also with the sulphuric, which last can never be concentrated singly to a greater degree than that at which it retains as much water as contains oxygen equal to half the sulphur in the acid itself, this being the proportion required in the bases saturating this acid as has been already fully described. Hence the impossibility of forming sulphuric acid by the combustion of sulphur in dry oxygen without the presence of water; and hence when the dry sulphats, such as alum, are distilled *per se*, the product is not sulphuric acid, but only its elements sulphureous acid and oxygen. The same takes place with the nitric acid, which can never be produced by the mere distillation of the dry nitrats that contain no water of crystallization, as these when heated yield only oxygen and nitrous acid gas till water be added.

Besides this *water of composition* there exists (often in the same compounds) another portion, which is the *water of crystallization*, and there seems some reason to infer from the author's numerous experiments, that the quantity of water of crystallization is such that its oxygen is always a multiplication or a division of

that of the base by an integrant number. Some of the experiments we shall mention.

*Tartaric Acid*, 160 parts of this acid well dried, were dissolved in water, and decomposed by acetited lead. The resulting tartrite of lead weighed 235.1. Five parts of this tartrite were then decomposed by sulphuric acid, and gave 4.23 of sulphat of lead, the composition of which being already known, that of tartrite of lead was inferred to be 164.87 oxyd of lead (containing 11.79 oxygen) to 100 of pure tartaric acid. Hence the 235.1 of tartrite of lead before mentioned contained 88.75 of tartaric acid free from water, and 11.25 of water; or, (in the same proportions) 100. parts of pure tartaric acid combine with 12.7 of water, containing 11.2 of oxygen. As this 11.2 does not very much differ from 11.79, it may therefore be inferred (making allowance for inaccuracy of experiment) that the water and the oxyd of lead saturating 100 parts of pure tartaric acid contain the same quantity of oxygen.

*Citric Acid*. 100 parts of dry citric acid were dissolved in water, mixed with 300. of oxyd of lead, evaporated to dryness and dried for some hours at a heat above boiling water. The residue weighed 379. parts, and hence there was a loss of water from the acid amounting to 20.85 per cent. Another 100. parts of the same citric acid combined with lead from the acetite, as in the foregoing experiments with tartaric acid, gave 237.56 of citrat of lead. Another 100. of the same citric acid heated on a sand bath till it first melted and then hardened,

Sulphuric acid	—	—	28.9	containing	17.34	oxygen
Suboxyd of iron	—	—	25.7	—	5.8	
Water	—	—	45.4	—	40.16	

therefore the oxygen of each of these three elements is respectively in the proportion of 1.3 and 7.

The author gives many other experiments on this subject from which he deduces the following law, namely, that in every compound of three or more oxydated substances, the oxygen of that constituent part which contains the least quantity of it is a common divisor for the other quantities of oxygen. And where one of the compounds is *water* its oxygen is equal to that of the base multiplied by some integral number. But it does not always happen that the oxygen in the water bears the same simple ratio to that of the acid; though each of them are measured by a simple multiplication of that of the lowest base. Thus in the case just stated, the oxygen

but without decomposition, lost 7.08 of water. 100. parts of the citrat of lead treated with sulphuric acid, gave 90.56 of sulphat of lead, which contain 66.66 of oxyd of lead, and hence the composition of citrat of lead is 1. of acid to 2. of oxyd of lead. From these data the inferences (which need not be gone over at length) are, that 100 parts of mere citric acid saturate as much oxyd of lead as contains 14.13 oxygen: that 100 parts of the crystallized acid contain 20.85 of water, 7.08 of which may be repelled by heat alone, and may therefore be considered as *water of crystallization*; and the remaining 13.77 is the *water of composition*, and the former is (within a trifling difference) half the latter. Moreover, 100. of real citric acid will unite to 17.14 of water of composition (which here acts the part of a base, as it is expelled only by displacing it by the intervention of another base) and this 17.14 of water contains 15 of oxygen; and this quantity of acid also combines with 8.52 water which contains half this quantity of oxygen. Hence (making large allowance for inaccuracy) the oxygen of the water of crystallization in citric acid being taken as 1. that of water of composition, and also that of the saturating portion of oxyd of lead are each about 2. which agrees with the law of composition laid down.

Many other saline substances examined by the author were found tolerably well to agree with the above law. For example, 100 parts of crystallized sulphat of iron contain the following elements, viz.

of the water is to that of the base as 7 to 1, and that of the base is to that of the acid as 1 to 3; but that of the water is to that of the acid as 7 to 3, which is a ratio that cannot be expressed by an integral number.

ALALITE. See AUGITE.

ALAUNSTEIN.

A specimen of this mineral was found by Klaproth<sup>a</sup> to contain

55.5	silice
19.	alumine
16.5	sulphuric acid
4.	potash
3.	water
—	
98.0	
—	

<sup>a</sup> Journ. de Phys. lxxi. 412.

From the concurrence of this analysis with that of Vauquelin, it may be concluded that the above are the ingredients which enter into the composition of the alum-stone of La Tolfa. The difference in the respective proportions obtained by these able chemists depends in part, no doubt, on a want of perfect uniformity in different portions of the mineral itself.

#### ALBUMEN.

Dr. Bostock has given some useful observations concerning this substance.<sup>a</sup> When white of egg is coagulated by heat and then long digested in water, about a fourth part is dissolved, the remainder being untouched. White of egg also loses about 80 per cent. of its weight by gentle drying, which loss appears to be pure water. When water containing only a thousandth part of pure albumen is heated to boiling its presence is indicated by a perceptible opacity. The *pure* albumen here mentioned is reckoned to constitute  $15\frac{1}{2}$  per cent. of the entire white of egg. A solution of albumen of the above strength is rendered milky by a few drops of corrosive sublimate solution, and after a while a curdy precipitate collects. Nitromuriat of tin has a similar effect but is not quite so powerful. Equal parts of an infusion of galls (half an ounce to half a pint of water) and a solution of  $\frac{1}{1000}$  of pure albumen form a precipitate after standing a time. Goulard's extract (a saturated solution of litharge in hot vinegar) precipitates albumen very speedily.

Most of these and other substances which coagulate albumen also act upon other animal fluids, but Dr. B. considers the coagulation by heat alone and by corrosive sublimate as exclusively belonging to albumen when compared with jelly and mucus. When corrosive sublimate is first added to a solution of albumen and heat afterwards applied, the coagulation is very complete, and the coagulum separable from a very dilute solution, but then it is a solid compound of albumen with oxyd of mercury. The solution of tan, though considered as the appropriate precipitant of jelly, will also affect a solution of albumen, though not to the same degree, and the compound precipitate of tan and the animal matter is not so dense and separable from the liquid when albumen is present.

Almost every metallic solution is precipitated by albumen,<sup>b</sup> and this precipitate then consists of acid, metallic oxyd and albumen, but it is again soluble more or less completely in an excess of albumen. Hence it may be inferred

that it is the albumen which holds in solution the oxyd of iron met with in the blood.

Mr. Brande has given some very valuable facts respecting the detection of small quantities of albumen by the galvanic action.<sup>c</sup> When the conductors from a galvanic battery are brought near each other in white of egg, an immediate and rapid coagulation takes place at the negative wire but only a thin film of albumen forms at the positive wire. This has been explained on an idea first suggested by Dr. Thompson, namely that the fluidity of albumen depends on the presence of alkaline matter, the separation of which at the negative pole causes the albumen to assume a solid form.

Pursuing this idea, Mr. Brande coagulated some white of egg by heat and then extracted by hot water that portion of the coagulum which (as observed by Dr. Bostock) is again soluble in water, this solution was then exposed to the galvanic action, and a copious coagulation took place at the negative pole.

The decomposition of liquid albumen by voltaic electricity takes place however in very different ways according to the power employed. When the power is comparatively high the coagulation goes on rapidly at the negative pole and only slowly at the positive; whereas with an extremely low power, the coagulation is comparatively rapid at the positive surface, whilst an alkaline solution of albumen continues to surround the negative pole. It would appear also that gelatine is not precipitated by galvanic action as albumen is; which may afford an useful mode of analyzing and separating a mixture of these two fluids, and also of distinguishing a solution of albumen in alkali (such as exists in the serum of blood) from real jelly, which, when concentrated, it resembles, in having a gelatinous appearance. Thus on mixing a solution of isinglass with serum of blood and exposing the mixture to galvanic action, the albumen of the serum was first separated by this means, after which an addition of galls detected the jelly of the isinglass apparently unaltered.

Professor Berzelius in his elaborate analysis of the blood<sup>d</sup> (which will be further noticed under that article) finds that a solution of albumen, such as exists in the serum of blood, will readily dissolve many metallic salts particularly the suboxyds of iron. This solution is readily made, and is green when the black oxyd is used and becomes yellow by exposure

<sup>a</sup> Phil. Journ. vol. 11. and 14.    <sup>b</sup> Thenard. An. Chim. tom. 67.    <sup>c</sup> Phil. Trans. for 1809 & 1812.

<sup>d</sup> Medico-Chirurgical Transactions, vol. 3.

to the air, with deposition of red oxyd. A mineral acid precipitates the albumen colourless and retains the iron in solution. The prussiates alone do not disturb the solution of iron in albumen, but on adding a little muriatic acid, an exquisitely beautiful blue precipitate falls down, which is a compound of Prussian blue and albumen.

The same author finds (as indeed has every other) that there appears to be very little difference between fibrin and albumen except in the mere circumstance that albumen does not coagulate spontaneously, and albumen seems to be intermediate between fibrin and the colouring matter of blood. The ash of coloured albumen is white; it contains no iron, but shews a little soda, phosphate, and carbonate of lime, and some magnesia.

The ultimate analysis of albumen when decomposed by combustion with oxymuriate of potash is thus given by Messrs. Gay Lussac and Thenard.<sup>a</sup> 100 parts of albumen supposed to be free from all earthy and metallic parts, contain,

Of carbon . . . . .	52.883
Of oxygen and hydrogen in the } proportions to constitute water }	27.127
Of hydrogen in excess . . . . .	4.285
Of azote . . . . .	15.705

---

100.000

The albumen here employed was white of egg, dried as much as possible in a boiling water heat. Sixteen grammes left after calcination in open fire 0.976 of a gramme.

In the results of this analysis of the proportion of its elementary ingredients it is found to agree most closely with fibrin. (See *Analysis in this Appendix.*)

#### ALCOHOL AND ETHER.

Muriat of lime affords a still better means of bringing alcohol to the highest degree of rectification than subcarbonate of potash, or it may be used after the alkali has ceased to exert its power. Dry muriat of lime added to alcohol already highly rectified will produce two liquors, the lowest a watery solution of the salt, the highest a spirit which when carefully decanted and redistilled at a gentle heat, will afford alcohol of extreme purity and strength, the first distilled portion is the lightest and therefore the purest.

An elaborate series of experiments on the ultimate analysis of alcohol and ether, has been undertaken by Th. de Saussure,<sup>c</sup> in methods

<sup>a</sup> Recherches Physico-Chimiques, tom. 2.

somewhat differing from that of Lavoisier. The operation of analysis consisted fundamentally in combining the alcohol with the utmost possible quantity of oxygen, so as to reduce it entirely into carbonic acid and water, (which indeed was that of Lavoisier) and calculating from the known proportions of these substances, those of the respective constituent parts of alcohol.

Several data must be laid down as elements of these calculations, and those assumed by M. de Saussure are the following:

100. parts of water contain by weight 88. of oxygen and 12 of hydrogen, 2. parts by measure of hydrogen saturate one measure of oxygen to form water.<sup>b</sup>

1000. cub. inch. of hydrogen gas (Bar. 28°. Ther. 10°. Reau.) at the point of extreme dryness weigh 34.303 grs. (French weights & measures.)

1000. cub. inch. of oxygen gas under the same heat and pressure but at the term of ex-moisture weigh 512.37 grs.

1000. cub. inch. of carbonic acid, under the same circumstances as the last, weigh 693.71 grs.

Carbonic acid contains its own bulk of oxygen gas.

100. parts by weight of carbonic acid gas at the point of extreme humidity contain 26. parts of carbon.

The alcohol here used had the specific gravity of 0.792 at 16°. Reau. (68°. Fahr.) and was obtained by distilling common spirit of wine from half its weight of muriat of lime dried nearly at a red heat, and drawing off only half the liquor; and again distilling this from its own weight of muriat of lime and drawing only half.

This alcohol was burned in three different ways.

The first, (which was that of Lavoisier) was to burn it in a lamp under a receiver filled with oxygen gas.

The second, was to detonate its gaseous vapour with oxygen gas in Volta's Eudiometer.

The third, was to decompose it by passing it through a red hot porcelain tube.

The exact process of the first mode differed in some particulars from that of Lavoisier. From this the composition of 100 parts of the alcohol used was estimated as follows:

Carbon . . . . .	36.890
Hydrogen . . . . .	9.365
Oxygen and hydrogen as water	53.745

---

100.000

<sup>b</sup> I. Phys. tom. 64, or Phil. Journ. vol. 21.

Of the above 53.745 of water, the oxygen is 47.296 and the hydrogen therefore is 6.449, which added to the 9.365, gives 15.814 for the entire hydrogen.

As these results differed considerably from those of Lavoisier, M. de Saussure repeated the experiment with alcohol rectified by distillation alone without addition; but after making due allowance for the proportion of water in this lower alcohol (from Richter's tables) the composition of the pure alcohol contained therein, hardly differed from the former where this alcohol alone was employed. Hence the comparative accuracy of the experiments was proved, and also the important point was proved that alcohol thus highly rectified by distillation twice from muriat of lime, does not sensibly approach to the nature of ether, as has been supposed.

The second mode of analysis was by detonating the vapour of this alcohol with oxygen in Volta's tube by the electric spark. This however would not detonate without the mixture of a little hydrogen. The fumes left after the detonation had no smell of burning spirits. After all calculations the composition of the alcohol from this experiment is:

Carbon . . . .	42.82
Hydrogen . . . .	15.82
Oxygen . . . .	41.36
	<hr/>
	100.00

The third mode of analysis was by passing the alcohol through a red-hot tube and examining all the products, an operation of great length and very complicated. Several foreign substances were thus detected in the alcohol, such as potash, lime, siliceous and acetic acid, but in very minute quantity. The *immediate* products of the whole process were a carburetted hydrogen gas, water, oil, charcoal and ashes. Of these the gas was in by far the greatest proportion, and was analyzed separately.

The composition of alcohol derived from this last process, agreed very nearly with the last mentioned, it was:

Carbon . . . .	43.65
Oxygen . . . .	37.85
Hydrogen . . . .	14.95
Nitrogen . . . .	3.51
Ashes . . . .	0.04
	<hr/>
	100.00

This result however shews a small propor-

tion of nitrogen which escaped notice in the former experiments.

*Sulphuric Ether.* This fluid was analyzed also by M. Theod. de Saussure, both by transmission through a red-hot porcelain tube, and by the detonation of its elastic vapour. In the former method the ether was entirely decomposed and the immediate products were a large quantity of oxycarburetted gas, amounting to near nine tenths of the weight of the ether, some oil and some charcoal deposited in the tube.

The ultimate analysis of ether gave the following results:

100 parts of ether contain	
Carbon . . . .	59.
Oxygen . . . .	19
Hydrogen . . . .	22
	<hr/>
	100

Hence in equal weights ether contains much more carbon and hydrogen than alcohol, but less oxygen. The author endeavoured to ascertain what quantity of ether a determinate weight of alcohol would produce. By distilling alcohol first with sulphuric acid and then rectifying the residue by several alternate distillations from a solution of potash and fresh sulphuric acid, he obtained from 100 parts by weight of common spirit of wine, 25.25 parts of ether in the first process; 10.3 in the second; and 3.2 in the third, reckoning as part of the product the actual loss of weight during each distillation, which is here considered as etherized vapour. The sum of these products and losses of ether amounts to 38.75, which is nearly half the weight of the pure alcohol contained in the 100 parts of the common spirit of wine. These experiments, like most of the others made on these substances with a view of analysis, are confessedly only approximations to accuracy, being laborious and complicated.

*Nitric Ether.* An elaborate and important series of experiments on this and many other ethers has been performed by M. Thenard,<sup>c</sup> from the particulars of which the following description of its properties is deduced.

Nitric ether is a very inflammable, odorous, pungent liquid, somewhat lighter than alcohol, and soluble in this fluid in all proportions; almost insoluble in water, though when mixed with it giving it the smell of rennet apples; decomposable by heat and forming nitrous and acetous acid; soluble in every gas, and with

the nitrous and acetous acid gasses, producing a most intimate combination which can with difficulty be separated by alkalies. Nitric ether reduced to its ultimate elements is thus composed:

Azote . . . .	14.49
Carbon . . . .	28.65
Oxygen . . . .	48.52
Hydrogen . . . .	8.54
	<hr/>
	100.00

Nitric ether is obtained by distilling equal parts of highly rectified alcohol and nitric acid. 1000. parts of the mixture give about 160 of pure ether, but for this purpose the gaseous product, which is very abundant, must be passed through five or six bottles half full of saturated brine, and cooled by ice or snow and salt, or some similar freezing mixture; and the retort itself must be frequently cooled with cold water to moderate the action of its contents. All the ethereal liquors contained in the bottles must be then collected and freed from their acid, by being shaken in a bottle in contact with lime.

The gas disengaged by the first distillation is very abundant, and consists of much nitrous oxyd, a little nitrous gas, azote, nitric, acetic, and carbonic acids, together with a good deal of ether, most of which however is separated by the intense cold of the apparatus.

If the distillation is stopped when no more ether is given over, the residue contains nearly three fifths of the whole mixture, and is yellowish, acid, alcoholic, and contains nitric and acetic acids.

Nitric ether, or etherized nitrous gas, may be decomposed by potash, in the latter case by frequent agitation with a solution of the alkali, in the former by being added to an alcoholic solution of potash. After a day or two the decomposition is compleat, and the residue contains alcohol, nitrite and acetite of potash.

*Muriatic Ether.* The properties of this ether have also been examined by M. Thenard. Muriatic ether may be made in various ways, with more or less ease, both by distilling alcohol and the metallic muriats, and also by the direct union of muriatic acid and alcohol, as we have mentioned in the Chem. Dictionary. M. Thenard prepared it in the following way: equal volumes of alcohol and muriatic acid both highly concentrated, were put into a retort (with a few grains of sand at the bottom to avoid the spirting up of the contents when

boiling) and well shaken, and then set over a furnace. A tube of safety connected the retort with a tubulated receiver, double the size of the retort, and partly filled with water so as to immerse the end of the tube. Another tube proceeded from the receiver to the first of a series of bottles also filled with water. The retort was gently heated, and bubbles of etherized gas soon appeared, mixed with some alcohol, acid, and water, all of which last were detained in the receiver, whilst the pure gaseous ether passed on in great abundance in proportion as the water became saturated with it. This gas is colourless, strongly ethereal to the smell, and tastes saccharine, particularly when dissolved in water. It has no action on litmus, violets, nor lime-water. Its sp. gr. is 2.219 at 64° Fahr. (common air being 1.00) and at a medium pressure and the above temperature is soluble in its own bulk of water. It becomes liquid at 52° Fahr. and hence the liquid ether may easily be obtained separate, by conducting the gas into an empty vessel surrounded with ice. The liquid ether also has no effect on litmus. Its specific gravity at 41° F. is .874. When poured on the hand it immediately boils and evaporates, producing much cold. It does not congeal at — 20° F. At a medium temperature and in a short time this ether, whether gaseous or liquid, shews no trace of muriatic acid either by the action of alkalies or by nitrat of silver; but the moment that this ether is burned, so large a quantity of muriatic acid is set at liberty as to diffuse its suffocating vapour all around and to be manifested by all the proper chemical tests. It is therefore a peculiar property of this ether to contain a large quantity of muriatic acid in a state which is not readily detected except by combustion.

Muriatic ether, both liquid and gaseous, is slowly absorbed by a solution of potash in water or in alcohol, at a low temperature. At first no muriatic acid appears to combine with the alkali, but after a considerable time a little of the acid separates, though partially, and becomes sensible by the test of nitrated silver. But by raising the temperature this separation of the acid becomes much more rapid.

The sulphuric and nitric acids in like manner have but little action on the ether when cold, but decompose it rapidly when heated. On the other hand oxymuriatic gas and muriatic ether, act upon each other immediately at a common temperature, and a large quantity of muriatic acid appears.

Some experiments have been made with the same view as those above mentioned, by M. Boullay.<sup>d</sup> The muriatic ether was prepared in the following way. Muriatic acid gas, disengaged from dried common salt and sulphuric acid, was passed through 1000. parts of pure alcohol by a suitable apparatus, and 680 parts of the acid gas were absorbed, during which the temperature (at first 50° F.) was raised to 75° F. The alcohol thus saturated with muriatic acid gas was colourless, of an oily consistence, of 1.134 sp. gr. smoking when exposed to air, miscible with water, but with the disengagement of heat and bubbles of air smelling strongly of ether. This muriated alcohol was distilled separately, and the products received first into an empty bottle, kept at the temperature of 14° to 17° F. by muriat of lime and snow, and beyond this, into water. The distillation from the retort took place at about 86° and most of the etherized gas condensed in the empty bottle into a liquid, which after washing with potash appeared to be pure muriatic ether.

M. Thenard states in a note (Mem. Arcueil, tom. 1. page 154) his surprize at learning that his experiments on the production of muriatic ether by muriatic acid and alcohol alone, which he considered as nearly original, had been anticipated by Basse, a chemist of Hameln, who prepared the ether by sulphuric acid, alcohol, and common salt, and by Gehlen who had repeated Basse's experiment. It appears however that Scheele discovered most of the remarkable properties of this ether, and pointed out its gaseous form, its peculiar sensible qualities, its giving no indication of acidity by litmus or nitrat of silver *before* combustion, but abundantly *afterwards*.

Muriatic ether is also made (as mentioned in the Chem. Dicty.) by distilling some of the metallic muriats or *butters* with alcohol, a process described by Scheele, Rouelle and Courtauvaux. This was repeated by Thenard with a little variation. A mixture was made in a retort of 7 parts of highly rectified alcohol and 12 parts of muriat of tin. A tubulated long-necked matrass was connected with the retort, and a Woulfe's apparatus was annexed. The matrass was empty and kept cool, the other bottles were full of water. On mixing the materials, a hissing noise like the quenching of hot iron in cold water was heard, and a very great heat was excited. The distillation was continued at a boiling heat till nearly all the

alcohol was driven over. No gas whatever was generated. In the retort was left a hard yellow muriat of tin; the matrass contained two strata of liquids, the lower, which was in small quantity was a solution of muriat of tin; and the upper was a thick liquid strongly ethereal and alcoholic, with a sharp metallic taste, reddening litmus, and depositing oxyd of tin on saturation with alkali. This liquid was diluted with water and redistilled, and the products were alcohol, etherized gas and muriat of tin. The etherized gas on further examination was nearly, if not absolutely, identical with the gaseous muriatic ether obtained by the former processes.

M. Thenard in a subsequent memoir gives his experiments on the ultimate analysis of muriatic ether, though confessedly imperfect. An essential part of this inquiry was to discover the proportion of muriatic acid, or its elements, combined in the ether. For this purpose a given quantity of muriatic acid and alcohol were put into a retort and distilled, with proper precautions to collect all the products, liquid and gaseous, and these were afterwards separately examined. The quantity of muriatic acid entering into the composition of the ether was estimated by comparing the quantity of potash required to saturate the acid in the retort before and after the distillation, all the loss of acid from the retort being supposed to enter into the composition of the ether. From these data it would appear that muriatic ether contains full 30 per cent. of its weight of muriatic acid of an equal degree of concentration as exists in fused muriat of potash.

#### *Action of Oxymuriatic Acid upon Alcohol.*

The mutual action of these two substances was first examined by Scheele, and afterwards by Berthollet, Pelletier, and other chemists. They have noticed the production of a green oil in the process, and of a quantity of ether. M. Thenard in repeating this experiment employed 300 parts of alcohol, and passed through it the oxymuriatic gas arising from 1750 parts of common salt, 450 of black oxyd of manganese, and 800 parts of sulphuric acid diluted with as much water. The gas was first washed by transmission through water, and then sent into the alcohol, and the whole was absorbed. The liquor contained a greenish-white oil, and a great excess of muriatic acid. On rectification with alkali no ether was obtained, but only an alcoholic liquor holding more of

<sup>d</sup> Ann. Chim. tom. 62.

the same oil in solution. This in some respect agrees with the result of Dollfuss's experiments before mentioned; <sup>e</sup> so that it seems still doubtful whether true muriatic ether is formed by the mere transmission of oxymuriatic acid through alcohol.

*Phosphoric Ether.*

The following process is given by M. Boullay <sup>f</sup> for the preparation of phosphoric ether, the existence of which had been doubted by several chemists. To a tubulated retort placed on a sand-bath was joined a tubulated receiver connected with a Woulfe's bottle full of lime water and with a pneumatic apparatus. Into the retort were put 500 grammes of pure phosphoric acid, made by acidifying phosphorus by nitric acid, vitrifying the acid, redissolving and evaporating it to the consistence of honey. A glass vessel similar to the *Acid-Holder*, open at both ends and terminating at one end in a long tube with a stop cock, was fitted to the tubulure of the retort, the lengthened tube dipping into the phosphoric acid. The receiver being kept cool by a mixture of salt and ice, the acid in the retort was heated to about 245° Fahr. Then 500 grammes of alcohol were let down, drop by drop, into the heated phosphoric acid. A violent ebullition took place on the mixture, which turned black, and numerous streaks of condensed vapour immediately appeared on the neck of the retort. The fire was kept up till the contents of the retort were dry.

There passed into the receiver,

1st. 120 grammes of weakly etherized alcohol.

2d. 260 grammes of a clear, light liquid, smelling much more strongly etherized than the last.

3d. 60 grammes of water saturated with ether, on which floated about four grammes of a yellow empyreumatic liquid resembling oil of wine.

4th. Another liquid insupportably fetid, reddening litmus and effervescing with carbonat of potash. When saturated with this alkali it afforded acetite of potash.

The lime water became turbid only at the end of the distillation.

The gas collected had a sweet penetrating smell, burning with a white flame and depositing a copious black soot.

The two first products of the distillation being mixed and rectified by gentle distillation from muriat of lime, gave 60 grammes of a

very pure ether strongly resembling sulphuric ether, in its partial solubility in water, rapid evaporation in the air, burning with a white flame and smoke, and leaving no marks of acidity when kindled on the surface of water.

*Alcohol and the Vegetable Acids.*

Most of the vegetable acids dissolve in alcohol, but the spirit is separable again by distillation in an unaltered state from all but the acetic acid, and even this latter will not convert alcohol into ether without frequent cohobation, or the use of some of the dry acetites.

But if a small portion of any of the concentrated mineral acids be added to the vegetable acid and alcohol before distillation, a most striking difference of result is observed. The alcohol is changed more or less completely into an ether or a substance resembling ether, consisting of an intimate combination of the alcohol and acid, which hardly if at all shews any acid properties before combustion, but gives a large quantity of acid afterwards. This curious subject was first undertaken by Scheele, who shewed by experiment the facility with which the addition of a little muriatic acid promotes the separation of acetic ether from acetic acid and alcohol, and observed a singular product obtained in this method from benzoic acid, muriatic acid and alcohol, but failed in procuring any particular results from the tartaric, citric, boracic and succinic acids. This subject has also been examined with some minuteness by M. Thenard. <sup>g</sup>

Some of the experiments we shall mention.

*Benzoic Acid, Alcohol and Muriatic Acid.*

30 parts of benzoic acid, 60 of alcohol, and 15 of concentrated muriatic acid, were distilled till two thirds of the ingredients had passed over. No gas but common air appeared, and scarcely a trace of muriatic ether. The first distilled product was only alcohol, but afterwards a peculiar matter came over dissolved in the spirit but separable by water. The retort also contained much of the same substance which had congealed to the bottom. It was separated from all the other matters by washing with hot water in which itself was hardly soluble. This substance was yellowish, pungent, somewhat heavier than water, fusible at from 76° to 86° F. and volatile at about 176° F. it was acid, oleaginous, nearly insoluble in cold water, but considerably soluble in hot water and in alcohol, from which last it was precipitable by water. When the excess of

<sup>e</sup> Chem. Dict. article *Ether*.    <sup>f</sup> An. Chim. tom. 62, p. 192.    <sup>g</sup> Mem. Arcueil. tom. 2.



acid was saturated with an alkali it still remained white, pungent, and odorous, and quite liquid at a common temperature. When long agitated with liquid potash it gradually was absorbed without the disengagement of any gas, and appeared to be resolved into alcohol and benzoic acid, but no muriatic, and yet it cannot be formed by the direct distillation of benzoic acid and alcohol, without the intervention of the muriatic acid.

The citric, oxalic, and malic acids, distilled with alcohol and a little sulphuric acid, all gave a peculiar substance somewhat resembling that from the benzoic acid.

*Acetic Ether.* 20 parts of acetic acid congealable at 52° F. were distilled once with 50 parts of alcohol of .800 sp. gr. It required much heat to bring the mixture to boiling, and only a very little acetic ether was produced.

The same experiment was repeated with the addition of 5 parts of strong sulphuric acid: 19 parts of the acetic acid disappeared, the ether was produced with singular ease and almost without heat, and as much as 40 parts were obtained: this appears to be a very simple and excellent process, and the ether may be rectified easily by a little potash even without a second distillation.

Acetic ether may also be made very well by Scheele's method, (*Chem. Dict. art. Ether.*) The following are given by M. Thenard as good proportions: 3 parts of acetate of potash, 3 parts of strong alcohol, and 2 parts of concentrated sulphuric acid, distilled to dryness. The product again slowly distilled with a fifth of its weight of fresh sulphuric acid, will give as much rectified acetic ether as the alcohol employed. The sulphuric acid should be always concentrated. Any other neutral acetite will answer the same purpose, and the dose of sulphuric acid should be somewhat more than will saturate the base of the acetite. The neutral acetites distilled *per se* yield a peculiar substance called *Pyro-Acetic Spirit*, already described in the article *Acetic Acid* in this appendix. M. Thenard infers as a general law, from these and other experiments, that when the vegetable acids are pure, none of them, except the acetic, will combine with alcohol in such a way as to lose their acid properties; but when a mineral acid capable of strongly condensing alcohol is added, all these vegetable acids acquire the property of uniting with alcohol into a peculiar compound which shews no acidity till the compound is again

decomposed by heat or alkalis, and which does not contain any of the mineral acid necessary to its formation.

*Alcohol—how produced from fermented liquors.*

In our original article (*Fermentation, vol. 1. p. 431*) we mentioned that a question has arisen whether alcohol exists ready formed in fermented liquors, or whether it is a product generated from them by the act of distillation. Mr. Brande has given some experiments on this subject in which he favours the former opinion.<sup>b</sup> Fabbroni who advanced the latter of these two opinions, asserts that though dry carbonate of potash will not separate any alcohol from wine in its natural state, yet if as little as a hundredth part of alcohol is purposely added to wine, this addition will be made apparent by mixing dry subcarbonate of potash to the wine. Mr. Brande however did not find this to be the case with the wines which he employed; for when 4 oz. of the dry alkali were added to 8 oz. of port wine, both pure, and mixed with  $\frac{1}{5}$  of alcohol, no separation of spirit took place in either instance, but the mixture in both cases divided itself into two portions, the lower of which was a saturated solution of the alkali, and the upper was a gelatinous mass containing apparently all the colour and extract of the wine, uniformly and undistinguishably mixed with the spirit. Nevertheless as it was found that very exactly the same proportion of alcohol was yielded by pure wine, when distilled at different temperatures, (the boiling point being raised artificially in some of the experiments by adding muriatic of lime) the author conceives that this is a sufficient proof that the alcohol is not *formed* but merely *expelled* from the wine by distillation, since if it had been actually formed in the process, he supposes that a change in the boiling temperature must have influenced the product of alcohol in one way or other.

A much more satisfactory proof of this opinion with regard to the formation of alcohol is however furnished by the same chemist in his last paper, in which he first precipitates all the extractive and colouring matter from wine by the subacetate of lead, and *then* the addition of the alkali separates the alcohol from the wine thus clarified in a very distinct manner. One measure of a saturated solution of the salt of lead added to 8 measures of port wine, and shaken for a few minutes and thrown on a filter, gave a perfectly clear and colourless

<sup>b</sup> Phil. Trans. for 1811 & 1813.

liquid, from which on the addition of dry subcarbonat of potash the alcohol separated rapidly. Mr. Brande found by experiments with alcohol and coloured water, that this mode separated the spirit almost totally from the mixture, whence it is reasonable to infer that no spirit whatever is generated by distillation, but only expelled from the fermented liquor.

The subacetate of lead is prepared by boiling two parts of sugar of lead with one of finely powdered litharge, in six parts of water. It should be kept carefully excluded from the air which is constantly converting it to insoluble carbonat of lead. The effect of this subacetate in separating all vegetable matter from infusions of vegetables has been long noticed by Dr. Bostock and other experimental chemists.

ALCOHOL OF SULPHUR. See SULPHUR, ALCOHOL OF.

#### ALKALI (FIXED.)

Potash and soda prepared from the carbonats of these alkalis by lime, the caustic alkaline solution being evaporated to dryness, redissolved in alcohol, and again dried and heated to redness, have long been considered as being in as high a state of purity as can be produced by chemical means. See the Article (*Potash*) *Chem. Dict. Vol. II.*

But a most important discovery has lately been made which affects the results of all the analyses of the neutral salts with a basis of potash or soda, and indeed is peculiarly satisfactory, as it explains the anomaly, before unaccountable, of the great difference in the estimation of these salts when the experiments are made with the dry alkaline carbonats or the dry caustic alkali. The discovery is, that the caustic fixed alkali prepared with the utmost care and brought to a state of fusion in a red heat, is not the simple alkali, but contains a considerable proportion of *Water*, which cannot be expelled by any length of fusion, though it does not accompany the alkali when neutralized with an acid and again brought to the heat of ignition. Hence if in any analytical experiment a given weight of ignited caustic alkali is saturated with an acid, and the entire neutral salt thence resulting is ignited and weighed, it is obvious that if the caustic alkali employed be considered as mere alkali, the proportion of alkali in the neutral salt will be much overrated, and therefore the quantity of acid required to saturate 100 parts of the alkali will be estimated much lower than the truth.

This anomaly was very accurately stated and

its real cause suggested by M. Darcet, in a Memoir read at the French Institute, January, 1808.<sup>a</sup> The experiments of this eminent chemist are (in a few words) the following:—Some very pure subcarbonat of soda was prepared and saturated with a dilute sulphuric acid, containing exactly a tenth part of a pure concentrated sulphuric acid of 1.844 sp. gr. This subcarbonat was found by various analyses to consist of 63.61 of water: 16.04 of carbonic acid, and 20.35 of soda. A hundred grammes of this subcarbonat were exactly saturated by 347 grammes of the dilute sulphuric acid, equal to 34.7 of the concentrated acid; which would give 170.515 of the concentrated acid to saturate 100. of the mere soda in the state in which it exists in the carbonat. On the other hand 100. grammes of caustic soda prepared by alcohol and fused in a silver vessel at a red heat, saturated only 119.6 grammes of the sulphuric acid in one experiment, and 122.4 in another, making a difference of about 50 grammes of acid in the estimated quantity in the two cases. Hence it must follow that the soda prepared by alcohol contains only 71 to 72 per cent. of real alkali in that state in which it exists in the carbonat, both salts being equally ignited, and therefore that which has usually been considered as pure soda, is properly *Hydrat of Soda*, consisting of about 72 of pure soda and 28 of water.

The next experiments on this subject which we shall mention are those of M. Berthollet.<sup>b</sup> This eminent philosopher in his *Researches on the Laws of Chemical Affinity*, has taken much pains to determine the respective quantities of most of the acids and bases that saturate each other, and in this enquiry the composition of sulphat of barytes came under particular consideration, as it is a salt very commonly obtained in analytical experiments, and its insolubility renders it a very convenient basis of calculation.

It would appear at first to be a problem of no great difficulty to determine the elements of this salt, and yet the calculations of equally skilful and accurate chemists varied as much as to give a difference of from 67 to 75 per cent. in the proportion of acid, which is much too great to be accounted for from any of the common inaccuracies in chemical experiment.

On further examination M. Berthollet found the cause of this difference to be in the barytes used. He and M. Thenard employed barytes crystallized from its aqueous solution, evaporated to dryness, and strongly ignited. M.

<sup>a</sup> An. Chim. tom. 68.

<sup>b</sup> Mem. d'Arcueil, tom. 2. p. 50

Berthier, Richter, Bachelz, and other equally distinguished chemists used the barytes prepared from the nitrat of barytes by a strong heat, which destroys the acid and leaves the barytes pure. In the first instance the barytes was more easily fusible than the other, and when cold had the appearance of a semi-transparent glass. The barytes from the nitrat on the other hand required a much greater heat for its fusion, and in melting absorbed a little carbonic acid. By adding a little water to this barytes it became in every respect like the other. The barytes from the watery solution of this earth, was also strongly heated with iron filings in a porcelain retort, and gave out a large quantity of hydrogen. From these facts the author shews that the barytes from the aqueous solution is a *Hydrat* of Barytes, containing about 10 per cent. of water, and the purer form of barytes is that which arises from the calcination of the nitrat.

This discovery led the author to suspect that potash might retain water when heated *per se*, and give it up when it enters into saline combinations. The principal experiment is the following: Some potash was melted in a silver crucible whose weight was known, and kept in fusion till it exhaled white vapours, when the cover was lifted off. The crucible with its contents was weighed when cool, and 15.73 grammes of fused alkali were found to be contained in it. This was dissolved in muriatic acid, and the whole solution with the washings was carefully evaporated and ignited in a platina crucible, till the muriat of potash was in perfect fusion. When cold, the muriat of potash weighed 20.335 grammes, and produced with nitrat of silver 38.586 gr. of well dried luna cornea, which (reckoning 17.5 per cent. of muriatic acid in luna cornea) indicated 6.752 gr. of acid. Consequently the 20.335 of fused muriat of potash consisted of 6.752 of muriatic acid and 13.583 of potash; but 15.73 of fused caustic potash was employed, and hence the difference between 15.73 and 13.583 (2.147) is the quantity of water contained in the fused caustic potash, which gives the proportion of 13.64 of water in 100. of fused potash.

The existence of a large quantity of water of composition in fused potash is also shewn by heating the alkali strongly with iron filings in a porcelain retort, by which a prodigious quantity of hydrogen gas is given out.

It appears however that though fused potash

gives up a large quantity of its water of composition when neutralized by an acid, yet some water is still retained, at least by one or other of the component parts of the compound, for most saline bodies will give hydrogen when heated strongly with iron filings.

Messrs. Gay-Lussac and Thenard,<sup>c</sup> have also made several experiments to determine the quantity of water contained in fused caustic alkali prepared with alcohol. A portion of fused potash was carefully weighed in a closed vessel, it was then taken out, put upon a dish of platina, and introduced into a large glass globe nearly full of a measured quantity of carbonic acid, standing over mercury, so that the alkali did not touch any portion of the glass. The alkali was then heated very gradually, when it became white on its surface, softened, rapidly absorbed the carbonic acid gas, and in so doing such a quantity of water was disengaged as to trickle down the sides of the glass globe. The heat was very gradually raised to a cherry red. The water was then absorbed by blotting paper, and the remaining carbonic acid gas measured, and the carbonat of potash weighed.

A similar experiment was performed on fused soda.

The results of these were, that 100 parts of fused potash in combining with carbonic acid, give up 13.596 parts of water; and 100 parts of fused soda give up 22.166.

The next experiment was to combine the alkali with silex by fusion, forming a glass. A given weight of the fused alkali and ignited silex were put into a silver crucible, and some water added to promote an entire mixture of the ingredients, which was then slowly dried and ignited to redness for an hour. The result was a perfect glass, which was weighed. From this experiment, 100. parts of fused potash were found to contain 18.45 of water of composition, and 100. parts of fused soda contain 26.15 of water.

The third experiment was the following: A certain weight of fused potash and of fused soda were saturated with sulphuric acid and the quantity noted. On the other hand known quantities of potassium and sodium were exposed to a moist air in long narrow vessels, till they were converted into their respective alkalies, which were then saturated with the same sulphuric acid as that employed before. Hence supposing the alkali produced from the potassium and sodium to be pure, and free

<sup>c</sup> Recherches Physico-Chimiques, tom. 2.

from water of composition, and knowing the quantity of alkali produced by the alkaline basis, it was easy to compare the saturating powers of these alkalis with those of the fused potash and soda prepared by alcohol. From these data 100 parts of fused potash prepared by alcohol contain 20.72 of water of composition: and 100 parts of fused soda contain 23.89 of water.

The authors take as a mean from these experiments (rejecting the first as far as regards the potash as being imperfect) that caustic potash, prepared in the common way by alcohol, and fused at a red heat, contains a fifth of its weight of water; and fused soda a fourth.

We may observe however that these results differ much too widely to be a fair subject for taking an average, except in a very general way. Perhaps, too, it is impossible to fix precisely the quantity of water contained in the fused caustic alkali, as this may vary according to the heat employed and other circumstances. It shews however that this form of alkali is certainly a *Hydrat*, or one that contains a notable quantity of water of composition, and also that no great dependance is to be placed on the accuracy of any calculation on the proportions of the alkaline neutral salts, which is founded on the quantities of the Hydrated Alkali employed.

#### ALKALINE BASIS. POTASSIUM. SODIUM.

One of the most interesting discoveries of modern chemistry is the decomposition of the fixed alkalis which had often been conjectured to be of a compound nature, but no evidence of the truth of this opinion had ever been given till Sir H. Davy applied to this enquiry the astonishing powers of electro-chemical agency. The researches which he had made on the decomposition of acids and neutral salts by galvanic electricity were full of new and most interesting results, they pointed out a mode of chemical analysis far more powerful than any that had been hitherto undertaken, and the admirable skill in contriving experiments, and sagacity in deducing from them the general laws of chemical decomposition, enabled him to make the brilliant discovery which is the subject of this article. He conjectured that if a freed alkali was an oxyd of some unknown base, it was probable that when it was subjected to the action of opposite electricities, the oxygen of the alkali would be conveyed to the

positive pole, whilst the inflammable base would appear in a separate state at the negative pole.

Some difficulties arise at first in selecting a proper mode of conducting the experiment. When a solution of the alkali was used, the electric power was expended chiefly in the decomposition of the water present; and on the other hand, when the alkali was dry and fused at the time of applying the electric power, it was indeed decomposed, but the basis instantly burnt with a most intense light and flame, and could not be collected. The great difficulty in the experiment was that the alkali, when dried and fused, is a non-conductor of electricity; but it was found that slightly moistening the surface renders it a conductor, and in this state it readily fuses and is decomposed by strong electrical powers.

The basis of potash was thus discovered.<sup>a</sup> A small piece of potash which had been exposed for a few seconds to the atmosphere, so as to give conducting powers to the surface, was placed upon an insulated disk of platina, connected with the negative side of the galvanic battery in intense activity, and a platina wire communicating with the positive side was brought into contact with the upper surface of the alkali. A vivid action soon took place. The potash began to fuse at both points of contact; there was a violent effervescence at the positive surface, and at the negative there was no liberation of elastic fluid, but small globules having a high metallic lustre, exactly resembling quicksilver in appearance, were formed, some of which immediately after burnt with explosion and bright flame, while others remained being first tarnished, and finally covered by a white film on their surfaces. The gas liberated at the positive surface was found to be pure oxygen, and the globules were found by numerous experiments to be a peculiar inflammable principle, the *Basis of Potash*. The platina was in no way connected with the result except as a medium for the electric power, for the same effects were produced by substituting copper, gold, plumbago or charcoal.

Soda when acted on in the same manner gave a similar result, but it required a greater intensity of galvanic action to produce the *Basis of Soda*. With a good battery of 100 6-inch plates, the Basis of Potash could be obtained from pieces of the alkali weighing 40 or 50 grains, which made the distance between the opposite wires nearly  $\frac{1}{4}$  of an inch; but with the same galvanic power, pieces of soda

<sup>a</sup> Phil. Trans. for 1808.

not exceeding 15 or 20 grains could be used, making the distance between the electric poles not more than  $\frac{1}{5}$  or  $\frac{1}{10}$  of an inch.

The Basis of Potash has been named by the discoverer POTASSIUM, and the Basis of Soda, SODIUM, which term has been universally adopted.

The principal properties of POTASSIUM discovered by Sir H. Davy in his first series of experiments, are the following.

When exposed to the air a white crust rapidly collects on the surface, tarnishing its metallic lustre, and this continues to be produced till the whole is converted to this white crust, which is found to be pure potash. When globules of Potassium are confined in common air, or especially in oxygen, at a common temperature, the same crust is formed, but not being removed by deliquescence, the process is stopped, the interior part of the globule being protected by the crust of regenerated alkali from further change. But when the temperature is raised highly, a rapid and brilliant combustion takes place, and the whole is changed to solid dry potash. Oxygen gas alone is absorbed in this change, the azotic admixture being in no degree affected, and the weight of the potash considerably exceeds that of the potassium decomposed.

Potassium is a soft and malleable solid of the lustre of polished silver at 50° Fahr, at 92° it is hard, brittle, and exhibits in its fractured surface beautiful facets of a perfect metallic whiteness. At 60° it begins to soften and become pasty, and at 100° it is perfectly fluid, so that the globules will run together. At a red heat it is converted into vapour, but in close vessels it condenses unaltered on cooling.

It is a very perfect conductor both of heat and electricity.

One of the most remarkable circumstances relating to potassium is its very great levity. Though resembling the metals in outward appearance, in opacity and lustre, it is not only lighter than any of them, but even than water, ether, naphtha, or almost any known fluid. The exact determination of its specific gravity is attended with difficulty, but Sir H. Davy estimates it at about 0.6 (water being 1.)

The action of water upon potassium is very striking. When a globule of it is touched with a drop of water, it instantly burns with a bright flame and a solution of potash is left. If this simple experiment be performed on paper tinged yellow with turmeric, the spot where the combustion and generation of alkali takes place is

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strongly marked by a deep brick-red stain. When potassium is decomposed by water in close vessels, a gas is found among the products, which is pure hydrogen. So strong is the affinity of potassium for oxygen, that it decomposes water wherever it exists, and thus discovers the watery admixture in the purest alcohol and ether, in both of which the potassium produces potash and hydrogen gas.

In the liquid acids potassium is immediately decomposed. In the sulphuric it produces at once a white salt (probably sulphat of potash) with a yellow coating, which appears to be sulphur. In the nitric and muriatic acids it produces nitrat and muriat of potash.

As potassium cannot exist for a moment unaltered in water or any fluid containing water, nor for any length of time in air, it was a matter of difficulty to find some mode of preserving it. It was found however that naphtha recently distilled will preserve it unchanged for a sufficient length of time, though even in this fluid it gradually oxydates and forms a kind of potash soap with the naphtha, that collects round the globule and prevents it from floating in this fluid. It also slowly forms an alkaline soap when confined in any of the oils.

Potassium unites with many of the metals with great ease, forming very peculiar alloys. It amalgamates readily with mercury and remarkably reduces its fluidity; for when united with 30 times its weight of mercury, the alloy is hard and brittle. The fluid amalgam dissolves all the metals, forming a triple alloy of mercury, potassium and the other metal employed. When the amalgam is thrown into water, a hissing noise is produced, hydrogen gas is given out, potash is generated, and the mercury returns unaltered to its original state.

Potassium will equally well unite with gold, silver and copper, and it is equally separable from these alloys by mere moisture, which regenerates the alkali.

Potassium readily reduces many of the metallic oxyds, and when in excess it unites with the metal thus reduced.

It decomposes the metallic oxyds in flint-glass and green-glass at a low red-heat; but it also gradually changes perfectly unmetallic glass when heated in such vessels, slowly alkalizing itself and corroding the glass.

These are the principal properties of this singular substance as given by the illustrious discoverer in his first memoir on the subject, by which it appears that potassium has by far the strongest affinity for oxygen of any hitherto

B

known substance, and this renders it a most valuable reagent for a variety of interesting chemical decompositions.

Before we proceed with the other properties of potassium we shall describe another method of procuring this substance without the assistance of any galvanic apparatus, and in much larger quantity. This method was found out by Messrs. Gay Lussac and Thenard, soon after Mr. Davy's original discovery of potassium, and is described by them with much minuteness. It consists in heating iron filings to great intensity in an iron gun-barrel, and then passing melted potash through them. The potash is decomposed, a large quantity of hydrogen gas is given out, and the potassium is condensed at the further extremity of the apparatus. As this, though not very complicated, requires a good many precautions, we shall give the original process with minuteness.

*The materials.* Iron turnings are preferable to iron wire or nails, as they present a considerable surface and yet allow the alkali to pass freely through them. They should be broken down in a mortar, and any adhering oxyd sifted away. The choice of the alkali is not a matter of indifference. The common potash or pearl-ash always contains a small portion of soda, and hence the caustic potash prepared from it is mixed with a little soda, which causes an alloy of a small quantity of sodium with the potassium obtained. Therefore in delicate experiments of research the potash should be prepared from pure crystallized nitre and cream of tartar ignited together, or from calcined cream of tartar alone, which gives the purest potash known. The alkali should be made caustic with lime in the way mentioned under the article *potash*, (Ch. Dict.) and indeed the extraction of the alkali by alcohol is hardly required, but it should be kept at a red heat for some time just before being used, as the presence of much moisture defeats the object of decomposition of the alkali.

*The apparatus* consists of a gun-barrel A.B.C. (see plate, fig. 1 and 2.) which should be well cleaned within and then bent in two directions by being heated red-hot at the parts required. The middle of the barrel B.C. which is enclosed in the furnace, must be well covered with a very refractory lute, as it is to undergo a very intense heat for a considerable time, which would soon oxydate and destroy the barrel without such protection. The best lute

is a mixture of pipe clay (or Windsor loam) beat up with a little water, and incorporated with as much sand as possible so as to make it difficult to apply. The only part to be luted is that which lies across the furnace, and to this the lute is to be applied in three or four successive thin coatings, and dried with great care, first for a few days in the shade, and then with a gradual heat, filling up any little cracks in it by some fresh lute. The gun-barrel is then filled with the iron turnings, as far as from B. to C. and is then firmly fixed in the furnace, and afterwards the fragments of recently heated potash are put in, without being much pressed, so as to reach not quite to B. and up to a few inches below A. This requires generally about 3 ounces troy, more or less. As much gas always issues through the other extremity D, to prevent any mischief or loss of potassium when accidentally stopped up, it is of use to adopt a bent glass tube to the upper end of the barrel A. which dips under mercury M. as seen in the plate, fig. 1. and allows of the reflux of any gas from the barrel if necessary.

The apparatus being then put up, a fire is lit in the furnace, and the bellows applied at first very gradually, to prevent the lute from cracking. The recipient G. H. is formed by two copper tubes fitted to each other by grinding, the uppermost of them receiving the end D. of the gun-barrel. A glass tube F. fits into the lower half of the recipient and dips into mercury. The recipient is luted on to the gun-barrel by the same fire-lute. When the fire is well kindled the bellows are to be used vigorously, and the heat raised to a very high degree at the same time that the ends of the barrel that project beyond the fire above and below, are kept cool by wetted cloths. When the fire has been raised to its utmost for some time, the wet cloths are removed only from the upper end of the barrel that contains the potash, and instead of it either a small furnace, or chafing dish or hanging trough of iron, E. filled with hot charcoal, is to be applied so as to cover the lower part of that portion of the barrel that contains the potash, and to melt the alkali, which requires a moderate red heat. The melted alkali then falls down into the lower part of the barrel, which is intensely heated, and passes in the form of vapour through the iron turnings. At first the water which the alkali contains in abundance (though previously fused)

† Recherches Physico-Chimiques, tom. 1.

decomposes upon the iron turnings, and much turbid hydrogen gas comes over. At the same time however the potassium is produced and is also vaporized within the furnace, but immediately condenses, partly in the extremity of the barrel, D. and partly in the copper recipient, all of which are, as before, kept cool by wetted cloths. When the efflux of gas begins to slacken, an additional portion of potash is sent down, by shifting the hanging trough of charcoal a little higher, and so on till the whole has been heated almost to the extremity A. It is of importance not to send over too much alkali at once, as this would damp the heat of the iron turnings, and lessen the product of potassium, and this too is one reason why the potash is put in in large pieces. It is a sign that the operation is going on well when the product of hydrogen at the lower extremity is pretty steady and abundant, but not very cloudy. The distillation is terminated when all the alkali has been successively melted down, which takes about an hour from the time that the gun-barrel is first made white-hot, and it then only remains to collect the product, which requires a little dexterity and caution.

The potassium being volatile condenses for the most part in the end of the barrel at D. and thence falls down into the copper recipient G. H. where it solidifies. To collect it, remove the barrel when the distillation is over, stop the upper end A. with a little lute, and hasten the cooling of the barrel by stripping off the lute and wetting the outside, then pull off the copper recipient (immediately stopping the end D. of the gun-barrel that is thus exposed) separate it into its two parts, pour into each a little naphtha, and detach all the potassium with a knife, throwing it into a bottle of naphtha as soon as separated. As some of the potassium remains in the end of the gun-barrel nearest to the recipient, it is the best way to cut off that end with a file, (as the barrel will never serve for a second operation) and to push out all the potassium into oil with a solid mould made for the purpose. This is generally mixed with a little potash from which it may be freed by melting in oil and pressing the whole.

The product of two experiments is given by the authors, in which it appears, that in one, 70 grammes (about 18 drams troy) of potash was employed of which nearly  $\frac{4}{7}$  this was recovered undecomposed from the iron turnings, and the product of potassium was 15.5 grammes (231 grains troy.) In the other experiment

81. grammes of potash were used, and the product of potassium was 20. 2 grammes or nearly a third more than in the former case.

Sometimes the efflux of hydrogen gas from the lower part of the barrel ceases suddenly, and appears at the upper, extremity. This may be owing to the stoppage of the end D. by a collection of condensed potash, when the fire has not been kept hot enough or when the alkali has been sent down too fast. This may sometimes be removed by heating the tube with charcoal on the outside, and melting away the obstruction. But if no gas is sent out from either end, it generally shews that the barrel has partly fused down owing to some imperfection in the lute, in which case the process must be discontinued and renewed afterwards either with a fresh barrel or better luting. If a very large barrel is used, a fresh charge of potash may be thrown into the upper part, and the process kept up for an additional time provided enough of iron turnings are introduced at first.

After the operation, if the gun-barrel is divided in different parts where it has been exposed to the furnace, it is found to contain a very hard agglutinated mass of alkali, oxyd of iron, alloy of iron and potassium, and unaltered iron turnings, which require considerable digestion in water to dissolve out the alkali. The quantity of alkali recovered from the iron, is full half of what has been used, and yet a large portion of the iron turnings retain their metallic appearance and their form, so that there is probably much loss of potassium by its alloy with part of the iron, which returns to the state of potash when moistened.

It may be of some assistance to the chemical operator to give Dr. Henry's very clear directions for preparing potassium, according to a process just described, but with some little variation in the apparatus.<sup>c</sup>

The apparatus consists of a common gun-barrel, curved and drawn out at one end to rather a small diameter, (see plate, fig. 3). To one end is adapted an iron tube *a*. with an iron stopper) of the capacity of two cubic inches, for containing the potash. At the bottom of this tube is a small hole *h* through which the potash gradually flows. This tube is shewn separately in fig. 4. To the opposite end of the gun-barrel a tube of safety *e* is to be cemented; and into this a sufficient quantity poured either of mercury or naphtha. Into the gun-barrel  $2\frac{1}{2}$  parts of very clean iron turnings

<sup>c</sup> Elements of experimental Chemistry, 6th. edition, vol. 1.

are to be introduced and pushed on to the bent part *c*. The tube, carefully luted is then to be placed in a small furnace, nine or ten inches in diameter, and provided with a pair of double blast bellows, the pipe from which is shown at *f*. The next step is to insert the tube *a* in its place, after having put into it  $1\frac{1}{4}$  parts of pure potash recently fused. The whole apparatus should be perfectly clean, dry, and impervious to air. A strong heat is now to be excited in the furnace, and while this is doing, the tube containing the potash as well as the opposite end of the barrel should be kept cool by ice. When the barrel has attained a white heat the potash in *a* may be melted by a small portable furnace. It will then flow by the small hole upon the iron turnings. Much hydrogen gas will be evolved, and when this slackens we may remove the small furnace from beneath the tube *a* and increase the heat in the furnace *d*, in order to restore to the iron turnings at *c*, the temperature proper for decomposing more potash. These operations may be repeated alternately till no more gas is produced, but last of all the heat in the furnace should be strongly raised to drive off some of the potassium that adheres strongly to the iron turnings.

When the furnace is quite cold, the safety-tube *e* is to be removed, and its place supplied by an iron plug. If the end of the gun-barrel projecting from this side of the furnace has been kept carefully cooled during the experiment the metal will be found adhering to it in the form of brilliant laminæ. In order to extract it, the gun-barrel is to be cut off at the beginning of the part that has been kept cool, where the greatest quantity will be found. Another portion will be found close to the plug, and this adheres so slightly to the gun-barrel that the least effort serves to detach it. It is even partly oxidated by the air that enters on cooling the furnace, and when the whole is covered with naphtha the oxidized part is detached in laminæ, exposing a white and brilliant metallic surface. The potassium which is condensed nearest the furnace must be separated by a sharp chissel in the largest pieces we can possibly break off. In the middle of the gun-barrel we shall find an alloy of potassium and iron which becomes green on exposure to the air, the potassium returning to the state of potash.

The potassium prepared in this way if the alkali is pure hardly differs from that obtained

by galvanic electricity, except that its specific gravity is somewhat higher, being to that of water as 796. to 1000.

Having already described the leading properties of potassium as first observed by Sir H. Davy, we shall proceed to give an abstract of a very long and minute series of experiments on the same subject carried on by Messrs. Gay Lussac, and Thenard,<sup>a</sup> most of which furnish results very nearly similar to those of the eminent discoverer of the alkaline metals, but others are different and throw new light on the nature of these curious bodies.

*Action of Water on Potassium.*—When a little water is confined in a jar over mercury, and a portion of potassium is passed up (enclosed in paper) the potassium swims on the water, moves about and lessens rapidly, and soon disappears, leaving the water very alkaline, and a considerable quantity of hydrogen gas is produced. When this experiment is performed, merely by throwing some pieces of potassium on water they soon become red hot while decomposing on its surface, which forms an amusing experiment. To determine the exact proportion of hydrogen produced by the conversion of potassium into potash by means of water, a small iron tube was filled with 2.213 grammes of potassium, and covered with a glass plate, and thus introduced under a bell-glass full of water. The decomposition took place with great rapidity, and, when complete, the hydrogen was measured and found to be 0.666 litre at 15° centigrade therm. and 0.7455<sup>b</sup> metre bar. The experiment was repeated with the same result, whence it follows that 100 parts by weight of potassium absorb 19.945 parts of oxygen to pass to the state of potash; and hence 100. parts of potash consist of 83.371 of potassium, and 16.629 of oxygen. These proportions closely correspond with those given by Davy and Berzelius.<sup>b</sup>

Messrs. Gay Lussac, and Thenard give a simple method of dividing potassium into equal portions without the trouble and loss attending the process of weighing this decomposable substance, namely, by compressing it into a cavity made in a small block of brass, on which another block exactly fits so as to exclude every atom of potassium except that which fills the cavity. The quantity of hydrogen given by this portion of potassium in ten different experiments varied only from 78.5 to 79.4 measures, and hence assuming 79. as the average, and comparing this result with the former above mentioned

<sup>a</sup> Recherches.

<sup>b</sup> Ann. Chim. Tom. 80. p. 245.



(in which 2.213 grammes of potassium gave .666 litre of hydrogen) the weight of the portion of potassium filling the cavity in the brass was pretty exactly estimated at 0.0212 gramme. This quantity was therefore the standard of all the subsequent experiments.

*Potassium and Oxygen.* If potassium is confined in contact with oxygen at a common temperature and kept at rest for some days, it gradually loses its metallic appearance, and is converted entirely into a grey substance. But if the temperature is a little raised or the surface of the metal renewed, it takes fire and the combustion goes on rapidly.

*Oxyds of Potassium.* There are certainly two distinct oxyds of potassium, and probably three, namely, the suboxyd, the alkali, and the peroxyd.

The suboxyd is a bluish-grey very brittle substance, softer than wax, easily fusible, so inflammable as to take fire in oxygen or even in common air at about 70° Fahr. decomposable by water into alkali, and giving out hydrogen like potassium but in smaller quantity. It is therefore in a lower state of oxydation than the alkali. This suboxyd is produced by confining potassium for some days in an empty phial closed with a cork, the pores of which admit such a very gradual supply of air and moisture as suits the slow and inferior state of oxydation required. It appears however doubtful whether this suboxyd may not be a mixture of potassium and potash, and it has certainly not been obtained sufficiently uniform to allow of its precise degree of oxydation to be well ascertained.<sup>c</sup>

The second oxyd of potassium is the alkali itself, the composition of which has already been mentioned. This oxyd, the alkali, is always produced, whenever potassium or any of its oxyds come in contact with water. When produced from potassium or the suboxyd just described, an evolution of hydrogen attends the alkalization of the metal, owing doubtless to the decomposition of water: when produced by moistening the peroxyd, the generation of the alkali is attended with the evolution of that portion of oxygen which constitutes the difference between the alkali and the peroxyd, but in either case the contact of water and of potassium in any form determines the formation of the alkali. In this way of forming the alkali it always unites with that portion of water of composition (amounting to about 18 per cent.) which, as has been mentioned in the beginning

of this article, is inseparable from caustic potash prepared by watery solution, even when it has been dried by fusion in a full red heat, and constitutes not properly pure potash, but hydrat of potash. The pure potash can only be obtained by heating the yellow peroxyd to be now described.

The orange-yellow peroxyd of potassium is prepared immediately by igniting potassium in oxygen, or even in common air. The discovery of the real nature of this oxyd, and of its containing more oxygen than the alkali does, is due to the eminent French chemists already mentioned. There is however some difficulty in performing the combustion accurately. If the potassium is burned upon glass or platina, these are both attacked by the oxyd assisted by the great heat generated, and incorrect results follow. A support of silver answers better, though with some risk of its fusion, or as Sir H. Davy recommends, the potassium may be laid in a small dish of platina, coated over with melted muriat of potash, which is not acted on by potassium or any of its oxyds. The French chemists observe that much of the inconvenience of a platina support may be avoided by using potassium that has been in oil, as it then burns at a lower temperature, or still better by employing the suboxyd which inflames spontaneously in oxygen. They give the results of eight different experiments on the combustion of the same quantity of potassium in a glass vessel full of dry oxygen confined over mercury, the potassium being laid in some experiments on glass, in others on platina, in others on silver. The yellow oxyd thence produced was then thrown into water, by which it passed to the state of alkali, giving out all its excess of oxygen. There is so little agreement in these experiments as to the entire quantity of oxygen absorbed by the potassium, that the composition of the peroxyd cannot be deduced from them. The largest quantity of oxygen absorbed (which is obviously nearest the true estimation) was pretty exactly twice as much as that portion required to convert the given weight of potassium into potash, and the experiments were so far satisfactory, that after the yellow oxyd was plunged into water and had parted with its excess of oxygen, the remainder which entered into the constitution of the alkali was nearly the same in each experiment. This peroxyd is fusible at a lower heat than hydrat of potash, and crystallizes in laminae by cooling. The colour is yellow when pure but brownish when mixed with oxyd of

<sup>c</sup> Davy.

platina. When thrown into water it gives out pure oxygen gas, and passes to the state of potash as before mentioned. When it is heated very strongly upon a platina support protected by muriat of potash, oxygen gas is given out,<sup>c</sup> and there remains a grey difficulty-fusible substance, vitreous in its fracture which disssolves in water with much heat but without any effervescence, and renders the water alkaline. This grey vitreous substance is considered by Sir H. Davy as pure potash, free from water or any foreign body, and it is the only known method of obtaining quite pure uncombined potash.

This yellow oxyd has a very striking action on all combustible bodies, to all of which it affords its excess of oxygen: in doing so it returns to the state of potash, and the alkali thus generated often unites with some or other of the products. Some particulars of these experiments we shall mention.<sup>d</sup>

Phosphorus heated with the peroxyd in an atmosphere of azotic gas produced a very vivid combustion, so as to redden the whole of the platina capsule in which it was contained. The azote was unchanged. Part of the phosphorus was burnt and part only volatilized. The product did not effervesce with water and with difficulty dissolved in it, though the salts of lime and barytes gave considerable precipitates. The product of this combustion was probably subphosphat of potash.

Sulphur heated in like manner with the peroxyd gave a compound which no longer effervesced with water (and therefore contained no uncombined oxygen) and smelt of liver of sulphur, and at the same time gave a copious precipitate with nitrat of barytes, and hence contained a mixture of a little sulphuret of potash with much sulphat.

Charcoal and the peroxyd heated together gave carbonat of potash.

The following metals, namely, tin, arsenic, antimony, zinc, copper, bismuth, lead and iron, all in fine filings, were separately heated with the peroxyd. In all the peroxyd was reduced to the state of potash but with some variation in the attending circumstances. With the tin, antimony, and arsenic, there was a great disengagement of heat and light, particularly with the former, so that both the capsule of platina on which the materials were placed and the glass vessel that confined them were made red-hot. The zinc and copper were but feebly ignited, and

the bismuth, lead and iron not at all. The heat was applied in all these cases with a spirit lamp on the outside of the glass vessel. By putting the product in water all the metallic oxyds were obtained except those soluble in the alkali generated in the experiment.

The peroxyd and potassium heated together in the same way produced potash with much disengagement of light and heat.

The peroxyd was introduced into an atmosphere of hydrogen confined by mercury. No effect was produced at a common temperature, but on heating it a rapid absorption of gas took place with abundance of moisture which streamed down the sides of the vessel, the peroxyd whitened and gradually became changed into potash. No light was disengaged.

Phosphuretted and sulphuretted hydrogen heated with the peroxyd produced in like manner water and potash, and sulphuret and phosphuret of potash.

With ammoniacal gas and the peroxyd the products were water and azotic gas.

The peroxyd was heated with muriatic acid gas. Much of the gas was absorbed, drops of water trickled down the sides of the vessel, oxygen gas was given out, and yellowish white-muriat of potash was formed, but no oxy-muriatic acid, nor was any light produced.

With carbonic acid gas the peroxyd when heated gave out oxygen gas, and carbonat of potash was produced which strongly effervesced with acids, but no water was generated.

The peroxyd was heated with sulphureous acid gas and the experiment was conducted with much care. The gas was carefully dried and had the specific gravity of 2.2553 (common air being 1.) the quantity of it as well as that of the peroxyd of potassium was weighed, as also was each of the products after the experiments. As soon as the heat was applied a brisk inflammation took place and an abundant absorption of gas. Sulphat of potash was formed, and a little oxygen gas, but not a trace of aqueous vapour. The oxygen was then separated from the undecomposed sulphureous acid, and the weights of the two gasses, added to that of the sulphat of potash, were found to equal that of the sulphureous acid gas and of the peroxyd of potassium employed.

The peroxyd was heated in nitrous gas, but without any particular estimation of quantities. Much absorption took place, very red nitrous acid gas appeared, and a salt was melted to the

<sup>c</sup> Davy.

<sup>d</sup> Gay Lussac, and Thenard.

bottom of the retort which was nitrite of potash. Nitrous oxyd produced no alteration whatever on the peroxyd of potassium.

The peroxyd may be made by heating potassium either in oxygen or in nitrous gas or in nitrous oxyd. In the latter cases, the potassium becomes highly oxydated at first, but on continuing the heat, seems to return to the state of alkali, and nitrite of potash is formed.

The French chemists, whose experiments we are now describing, consider the peroxyd of potassium as containing three times as much oxygen as the quantity necessary to convert potassium into potash; so that if potash consists of 84 parts by weight of potassium to 16 of oxygen, the peroxyd of potassium will consist of 84 of potassium to 48 of oxygen, or 63.64 per cent. of potassium and 36.36 of oxygen.

*Potassium and Hydrogen.* These combine neither at a common temperature nor at a red-heat, but readily at an intermediate degree, such as is produced by a spirit-lamp. Potassium thus heated in hydrogen gas absorbs it rapidly, but gives it out again with equal ease when the proper degree of heat is exceeded. The actual quantity of hydrogen absorbed seems to vary considerably, but on an average it appears to be about a fourth of the quantity which would be produced by immersing the potassium in water. This Hyduret of Potassium is grey, unmetallic in appearance and infusible. It inflames in common air or in oxygen only when heated. It is entirely decomposed into hydrogen and potassium when heated *per se* in a close vessel, and when in contact with hot mercury it is still more rapidly destroyed, the hydrogen flying off and the potassium amalgamating with the mercury.

Phosphorus unites readily with potassium. This compound is made by introducing the two into a glass tube filled with azotic gas and gently warming them. But little light is given out. The phosphuret of potassium has an unmetallic appearance, is of a chocolate colour, and when thrown into water produces phosphuretted hydrogen gas, which sometimes but not always inflames.

Sulphur forms a very intimate union with potassium, and the combination takes place with much more heat and light than in the phosphuret, so as to endanger the glass vessel, unless the sulphur and potassium are placed upon a platina dish within the tube, which last should be filled with azote. This sulphuret is sometimes yellow, sometimes red. It has the

smell and taste of rotten eggs, is soluble in water without the production of any gas, but with acids it is readily decomposed with evolution of sulphuretted hydrogen gas.

When potassium is melted in sulphuretted or phosphuretted hydrogen gas, a sulphuret or phosphuret of potassium is formed, and the hydrogen remains pure.

*Alloys of Potassium and the Metals.*

Potassium very readily unites with many of the metals, as was first ascertained by Davy, and indeed this circumstance is one that is brought forward as an argument of the metallic nature of this singular substance. Some of these alloys, as described by the discoverer, we have already mentioned; the following experiments are given by M. M. Gay Lussac and Thenard. The alloys were made either by heating the substances in a small bent glass tube over mercury and filled with azotic gas, or by introducing the potassium into a small glass tube closed at one end, covering it with the metal in powder, then drawing out the other end of the tube over a lamp and sealing it hermetically, and finally uniting the metal and potassium by a due heat over lighted charcoal.

Potassium 2 measures, lead in powder 8 measures, gave a solid brittle fusible fine-grained alloy. Exposed to air it decomposed gradually, and in water, suddenly. In either case potash was produced and the lead resumed its metallic state. Potassium 2 measures, bismuth 8 measures, a solid brittle alloy in small facets: decomposed as the last. Potassium 2 measures, antimony 8 measures: this mixture alloyed with great ease, giving out light in the process: decomposed as above.

Potassium 2 measures, tin 7 measures. Some light is given out during the union, which requires almost red heat to be effected. This alloy must be made in azotic gas as it is immediately decomposed in the air. When the tin is in a less proportion than the above, the alloy generally takes fire the moment it is attempted to be pulverized.

Potassium and zinc alloy with difficulty on account of the volatility of the potassium at the heat required.

Potassium and mercury will unite in any proportions. When the former was to the latter as 212 by weight to 3069, the amalgam remained fluid at a mean temperature. With twice the above quantity of potassium much heat was excited on mixture, and the amalgam was solid at a common temperature and easily

crystallized. The crystallized texture was still more decided with three portions of potassium. These amalgams will take place without heat when the potassium is free from oil or oxyd on its surface and quite clean. They often occur accidentally by the fall of particles of potassium on the mercury bath, which, as soon as they touch the mercury, move about on its surface with great rapidity, and soon disappear by being absorbed by the fluid metal. Much heat is given out when potassium and mercury unite.

Potassium 2 measures, arsenic 6 measures. This alloy is easily made and much light is given out at the time, but instead of having a metallic lustre it is of a dull chesnut brown hue, and when in contact with water it gives out a much smaller bulk of hydrogen gas than the same quantity of potassium gives when alloyed with any other metal. This gas was therefore examined with more care. A bent glass tube was filled with azote over mercury and 2 measures of potassium, and a piece of arsenic were introduced into the tube and united by fusion. The azotic gas was not in any degree altered. Water was then thrown up which caused a brisk effervescence and the production of potash, and the alloy was entirely destroyed, leaving only a light flocculent matter like kermes. The water was boiled to compleat the decomposition of the arsenical alloy. The only gas produced was 82 measures of arsenicated hydrogen. This experiment was repeated many times with different proportions of potassium, the gas being always measured, and it was found to be pretty accurately in direct proportion to the quantity of potassium used: but it was also found that the same quantity of potassium which when unalloyed with arsenic gave 79 parts of pure hydrogen, would give only on the average 33.36 parts of arsenicated hydrogen. This led to the analysis of arsenicated hydrogen. This gas was prepared both by moistening the alloy of arsenic and potassium, and by adding muriatic acid to an alloy of 3 parts of tin and 1 of arsenic. A given quantity of this gas was confined in a glass vessel over mercury, in contact with a vessel containing tin which was kept in fusion for three quarters of an hour. This process extracted all the arsenic from the gas, which then returned to the state of simple hydrogen, as was determined by there being not the least deposition of arsenic on the sides of the vessel in which the gas was subsequently burned. From the result of several experiments which agreed

sufficiently well, it was shewn that 100 measures of arsenicated hydrogen expand to 140 parts after the extraction of the arsenic. But this circumstance would only account for part of the apparent deficiency in the quantity of gas produced by the action of water on the alloy of arsenic and potassium, for if 140 measures of pure hydrogen produce 100 measures of arsenicated hydrogen, 79 of hydrogen (the quantity produced by each measure of pure potassium) should give 56.4 of the arsenicated gas, whereas the quantity of the latter gas actually produced, was only 33.36. This therefore would imply some loss of hydrogen, or rather a condensation of it in some one or other of the products so as to prevent it from assuming a gaseous form, and this the authors with great probability suppose to be the case in the brown arsenical flocculi that remain after the action of water upon the arsenical alloy, which flocculent matter therefore will then be a *Hyduret of Arsenic*. The possibility of a solid compound of hydrogen and arsenic has also been inferred by Sir H. Davy, as a result of the following experiments on the action of tellurium and arsenic on potassium.<sup>d</sup> Arsenic being made the negative surface in a powerful galvanic action taken in water, became dark coloured and threw down a brown powder, at the same time giving off much inflammable gas. Also an alloy of arsenic and potassium being heated in ammonia produced a gas which was principally azote, and hence the hydrogen of the decomposed ammonia must have entered into combination with the arseniuret of potassium.

Potassium heated in arsenicated hydrogen (to return to M. M. Gay Lussac and Thenard) becomes immediately covered with a red crust, dense fumes condense on the sides of the vessel, the gas is suddenly decomposed, and therefore expanded, pure hydrogen appears, and the arsenic combines with the potassium into a solid arseniuret similar to that produced by the direct union of arsenic and potassium.

Potassium may be readily alloyed with iron by putting some iron turnings in the lower extremity of the gun-barrel that projects beyond the furnace (in the apparatus for obtaining potassium) instead of leaving it empty to receive the condensed potassium. In this case the iron being long in contact with potassium in vapour absorbs it, becomes flexible, and often quite soft, and is decomposable in air or water like any of the other alloys of this substance. With-

<sup>d</sup> Phil. Trans, for 1810, p. 27, &c.

out doubt the alloys of the other metals that require a high heat for their fusion might be obtained in this way.

*Potassium and Gaseous Oxyd of Carbon* have no mutual action at a common temperature, but when heated they readily decompose each other. About 200 measures of carbonic oxyd (obtained from iron filings and carbonat of barytes previously ignited strongly) were heated with a portion of potassium. On the first impression of heat the potassium became blue, but presently took fire, a great and immediate absorption of gas took place, carbon was precipitated, almost all the potassium was changed to potash and the whole gas disappeared except about twelve measures, which were afterwards decomposed in a similar manner by a fresh portion of potassium.

*Potassium and Metallic Oxyds.* It has been already mentioned that the celebrated discoverer of the alkaline bases ascertained the extreme affinity of potassium for oxygen in every combination, which therefore renders it a most valuable re-agent for an infinite variety of chemical purposes. Among these he discovered that many and probably all the metallic oxyds when heated with potassium, are reduced to the metallic state by yielding their oxygen to the potassium; and if the latter is in excess, the newly reduced metals will alloy with this excess, or will unite with the potash newly formed in case the metals are soluble in this alkali.

Similar experiments have been repeated by the above French chemists on a great variety of metals, and with the same general results. They were all performed in a small glass tube, one end open, the other closed. A layer of the metallic oxyd was first put in, and over it the potassium, well cleaned from oil by blotting paper, and upon this another layer of the oxyd. The tube was then heated over a fire as required. In almost all the cases the reduction of the oxyd was attended with light, and generally the potassium passed to the state of potash, and not to that of either of its other oxyds.

The particulars of these experiments need not be specified in this place.

*Potassium and the Mineral Acids.* Carbonic acid gas and potassium do not act upon each other at a common temperature, but at a heat approaching a cherry-red, the decomposition is rapid and complete. The approach to this is shewn by the potassium becoming blue. It then takes fire, and the gas is ab-

sorbed almost entirely, leaving a little residue of carbonic oxyd, and an abundance of carbon precipitates. The potash thus generated is partly carbonated.

Potassium and sulphureous acid act on each other when heated, the gas is almost totally absorbed if the potassium be in sufficient quantity, and the solid residue is sulphuret of potash.

In nitrous acid gas potassium inflames even at an ordinary temperature, and burns with a red flame.

With oxymuriatic acid gas the appearances are nearly similar. The potassium burns with a red flame, and muriat of potash is produced.

When potassium is heated with muriatic acid gas, hydrogen is disengaged, and solid muriat of potash results. The quantity of hydrogen is the same as would be given out by the action of water on the potassium, and it is half that of the muriatic acid absorbed.

Vitreous phosphoric acid heated with potassium produces a pretty strong combustion, and red phosphuret of potash is left, which when wetted gives phosphuretted hydrogen not inflammable by exposure to air.

*Potassium and Alkaline, Earthy, and Metallic Salts.* The action of these substances was ascertained in the same manner as that of potassium on the metallic oxyds.

In all cases the potassium abstracted oxygen from those salts which are known to contain it, and the potassium was generally changed into potash, and not into either of its other oxyds. In many instances light was disengaged at the moment of mutual action. The salts employed were all previously dried as much as possible.

The sulphats heated with potassium were more or less perfectly converted into sulphurets.

The phosphats were in like manner changed to phosphurets, giving when moistened that species of phosphuretted hydrogen which is not spontaneously inflammable.

The carbonats with potassium were decomposed into carbonic oxyd, the base of the carbonat employed, and potash from the potassium.

Muriat of barytes and muriat of soda were not altered by potassium, which sublimed through them, being itself unchanged.

The fluats of soda and lime were equally unaltered.

Borax was unaltered by potassium.

#### SODIUM.

This substance was discovered by Sir H. Davy a few days after the discovery of potas-

sium, and by the same means, that is, by the electro-chemical action of a powerful galvanic battery acting on solid caustic hydrat of soda. The mode of preparing sodium therefore is precisely the same as that of potassium, substituting one alkali for the other. Sodium may also be readily prepared by igniting common salt and then heating it to redness with potassium in a close vessel. The salt is immediately decomposed, and the sodium rises very pure. No hydrogen is disengaged in this process, and two parts of potassium produce rather more than one of sodium.\*

Sodium is also prepared by the process discovered by Messrs. Gay Lussac and Thenard, for obtaining potassium, the apparatus being precisely similar, and no other difference being required than to substitute soda for potash as the alkali to be passed through the ignited iron turnings. As solid hydrat of soda contains much more water of composition than hydrat of potash, it should be kept for some time in fusion at a low red heat just before it is put into the gun barrel apparatus. In the distillation, a still greater heat is required to obtain sodium than potassium, and the transmission of the soda through the heated barrel should be slower.

Pure sodium is an opaque substance with a white silvery lustre. It melts at about 200° Fahr. if unalloyed with potassium, and it rises in vapour at a strong red heat. It is exceedingly malleable and soft like wax so as readily to be pressed out into thin leaves. Portions of sodium may easily be united into one mass by strong pressure, a species of *cold welding*. Sodium is a very powerful conductor of electricity. Small globules of it inflame by the Voltaic spark, and burn with bright explosions. The specific gravity is given by Davy at 0.9348 (water being 1.0) and by the French chemists at 0.97223.

Before we describe the chemical properties of sodium we shall notice its alloy with potassium, as this very materially alters its fusibility and specific gravity. These two substances unite perfectly, and indeed the alloy is always produced whenever the soda employed for the production of sodium is mixed with any portion of potash. This is the case with all the common soda or carbonat of soda that is used when prepared from barilla, unless particular pains be taken to purify it by repeated solution and crystallization; so that where sodium is to be obtained directly from the de-

composition of soda, the alkali manufactured from common salt is perhaps the surest.

When the soda contains as little as five or six per cent. of potash the mixed alkaline metal thence obtained becomes fluid at a temperature little above that at which pure potassium melts, and when the alloy contains more potassium it remains fluid at a common temperature. Three parts of sodium and one of potassium from an alloy fluid at 50°, and which crystallizes into a bright brittle mass when surrounded by salt and ice. Even a thirtieth part of potassium in the alloy materially increases its fusibility.

An alloy of 10. parts of potassium and 1. of sodium is also fluid at 52°, and is lighter than rectified naphtha. These alloys therefore are in all cases more fusible than pure sodium, and often more so than pure potassium, and they are also always brittle and crystallizable. The alloys may be made either by heating the alkaline metals under naphtha, or even by simple pressure without heat. It should be observed that these alloys are gradually oxydated even under naphtha when exposed for some time to the air, and that it is the potassium which first undergoes this change, and by this means sodium may be purified from a small admixture of potassium, the latter being entirely oxydated before the former is altered.

When sodium is exposed to the atmosphere it immediately tarnishes and gradually becomes covered with a crust of soda which deliquesces. Sodium confined in oxygen gas combines with it slowly and without any luminous appearance at a common temperature, but when heated it burns with a very white brilliant sparkling flame. In common air the flame is yellow.

When sodium is thrown on water it produces a violent effervescence of hydrogen with a hissing noise, the globules run about in all directions on the surface of the water, rapidly lessen without flame or explosion, and gradually disappear, leaving the water alkaline by the soda produced. The quantity of hydrogen produced by a given weight of sodium in water is thus given by Messrs. Gay Lussac and Thenard, whose experiments very closely coincide with the results adopted by Sir H. Davy. The mode of conducting the experiment was exactly the same as with potassium. 2.486 grammes of sodium decomposed by water gave 1.2525 litres of hydrogen gas at 15° centigrade Th. and 0.759 metre Bar.; whence it follows that 100. parts

\* Davy.

by weight of sodium absorb 33.995 parts of oxygen during its conversion into soda, and therefore 100. parts of pure soda free from all water of composition, contain 74.63 of sodium and 25.37 of oxygen.

The numbers adopted by Davy<sup>b</sup> are 88 of sodium to 30 of oxygen (88 being the number representing one proportion of sodium) which would give 74.5 per cent. of sodium and 25.5 of oxygen.

*Oxyds of Sodium.* The oxydation of sodium seems in every respect to run a parallel course with that of potassium.

There are three oxyds of sodium known, of which the alkali soda is in the intermediate degree of oxydation.

The suboxyd of sodium is formed like that of potassium by very slow circulation of air in a vessel confined by a cork. This suboxyd is grey, brittle, unmetallic in appearance, and gives out some hydrogen when moistened, but less than sodium.

The pure alkali Soda, free from water of composition forms the next oxyd of sodium. Its composition has just been mentioned. It is formed, like the pure potash, by heating the peroxyd. When produced by the action of water on sodium it always retains a considerable portion of water which is not expelled even at a red heat.

The peroxyd of sodium is formed as the peroxyd of potassium by heating the alkaline basis in oxygen gas. Its natural colour is a dirty yellow; but brown when prepared upon uncovered platina. When thrown into water it is immediately decomposed and passes to the state of alkali, giving out oxygen gas.

The experiments made by the French chemists to find the utmost quantity of oxygen gas absorbed by the combustion of sodium, in no degree accord with each other, except to shew that the term of oxygenation that produces the alkali is pretty accurately defined.

But beyond this, the excess of oxygen absorbed to produce the peroxyd (and which excess is given out when water is added) varies so much in the experiments given that no accurate inference can be made. The utmost quantity of this excess is somewhat more than half the quantity of oxygen absorbed to produce the alkali, and this proportion is also given by Sir H. Davy. Hence it may perhaps be allowed that sodium with two portions of oxygen becomes soda, and with three portions the peroxyd.<sup>c</sup> We may add that a very considerable

error has crept into the calculations of these eminent chemists from their own data. The quantity of oxygen absorbed by one measure of sodium is *not* 148 of the measures used, but half this number, or 74. It is the hydrogen given out which is 148, and hence the oxygen absorbed would be half this quantity *in bulk*, or 74; and this too agrees with the other numbers of the table given, being pretty nearly the quantity left after the action of water on the peroxyd in all the five experiments.

The chemical properties of sodium and its oxyds so closely resemble those of potassium in parallel cases as to render a particular description unnecessary. In almost every instance sodium absorbs oxygen from every substance containing it (the oxyds of potassium excepted) and the peroxyd yields that excess of oxygen above the quantity necessary for alkalization to almost every substance which has an affinity for oxygen.

*Oxygenation of the common caustic alkalies by fusion.* After the discovery of the peroxyds of potassium and sodium it was natural to examine whether any process of superoxygenation of the alkalies in their common state (that is as *Hydrats*) ever took place, when they were kept in fusion at a red heat exposed to the atmosphere. At a common temperature it is obvious that the deliquescence of these alkalies would of itself prevent any higher degree of oxygenation; and as even at a red heat the water of composition entering into these alkalies is not driven off, it was doubtful whether this circumstance might not oppose the further absorption of oxygen. Messrs. Gay Lussac and Thenard however assert that when common caustic potash or soda, prepared by alcohol, is kept in fusion at a red heat in an open crucible of silver platina or earth, it absorbs oxygen and partly passes to the state of peroxyd, and will again give out oxygen gas on being dissolved in water. A silver crucible answers best as the alkali has no action on it. Potash oxydates sooner under these circumstances than soda, so that in eight or ten minutes of fusion its colour deepens and it gives out much oxygen when wetted. But when the alkali is combined with carbonic acid no such superoxygenation takes place by any length of fusion.

On the other hand they assert that the nitrats of these alkalies when thrown into a red hot crucible and kept long enough to be completely decomposed, very readily furnish the peroxyds of the alkaline bases.

<sup>b</sup> Elements.

<sup>c</sup> See Recherches, &c. par MM. Gay Lussac and Thenard, tom. i. p. 513.

ALLANITE.<sup>a</sup>

This mineral occurs in oblique tetrahedral prisms, the alternate angles of which measure 117° and 63°, or in compressed hexahedral prisms terminated by tetrahedral summits; it also occurs uncrystallized and then is either massive or disseminated being mixed with black mica and felspar. Its specific gravity as far as can be ascertained on account of the intimately intermixed mica, is between 3.1 and 4.0. Its colour is brownish-black; when bruised dark greenish grey. Externally it is dull. Internally it exhibits a small conchoidal fracture with a shining lustre between resinous and metallic. It is opaque, in hardness ranks between felspar and glass; is brittle and easily frangible. Before the blow-pipe it froths and melts into a brown slag. It gelatinizes in nitric acid, and loses about 4 per cent. of its weight by strong ignition.

The substances obtained from 100 parts of it on analysis by Dr. Thomson, are

35.4	silic
9.2	lime
4.1	alumine
25.4	per-oxide of iron
33.9	oxide of cerium
4.0	volatile matter

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112.0

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Allanite is a native of Greenland, but of its geological history we are as yet entirely ignorant.

ALLOCHROITE.<sup>b</sup> Splittriger Granat K.

The colour of this mineral is yellowish or brownish-grey. It occurs in opaque amorphous masses. Its fracture is uneven passing to splintery, with a slight degree of lustre. It gives sparks with steel, and is difficultly frangible. Sp. gr. 3.5. Before the blow-pipe it is fusible without addition into a black shining opaque enamel.

It has been analysed both by Vauquelin and Rose, with the following results:

V.		R.	
35.	—	37.	silic
30.5	—	30.	lime
8.	—	5.	alumine
17.	—	18.5	oxide of iron
3.5	—	6.25	oxide of manganese
6.	—	0.	carbonate of lime
<hr/>		<hr/>	
100.0		96.75	
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<sup>a</sup> Nich. Journ. xxix. 48.

<sup>b</sup> Haüy Tab. Comp. 57.

<sup>c</sup> An. Chim. Tom. 68.

This mineral is considered by Karsten as a variety of garnet, and in fact its analysis nearly coincides with that of melanite or black garnet.

It occurs generally in pieces covered by carbonate of lime, and by dodecahedral crystals which appear to be garnet. These dodecahedrons are implanted by their lower extremities in the allochroite, into the substance of which they appear to pass by insensible degrees. The carbonate of lime in Vauquelin's analysis is no doubt foreign to the composition of this mineral and is to be attributed to the calcareous spar with which it is mixed.

It occurs in the iron mine of Virums, near Drammen in Norway.

## ALOE.

Three analyses have been made of this substance, of which the following is an abstract.

The first we shall mention is that of M. Braconnot.<sup>c</sup>

Aloes is a dark brown semi-transparent extract, easily reduced to powder, and very bitter, prepared from the natural juice of several species of the aloe plant, either by natural or artificial heat. The finest species is prepared only by inspissation in the sun's heat. The finest sort was selected for the following experiments:

50 grammes were heated *per se* in a retort, with a heat at first very gentle, and afterwards increased. The first product was a water loaded with the flavour of aloes, then a colourless water holding some acetous acid but no ammonia: then a red oil soluble in alcohol; and then at a higher heat much carburetted hydrogen with oil. The coal contained no potash.

Aloes rubbed in a mortar with water produces a viscous mass like turpentine when pressed with the fingers. A large quantity of water however dissolves the whole, excepting a little woody impurity, and the solution of the last portion is as bitter as the first. By heating the water, the solubility of aloes is greatly increased, and the hot saturated solution will assume somewhat of a crystalline form by cooling. The watery solution of aloes reddens litmus. Its colour is rendered deeper by lime-water and the alkalies, but nothing is precipitated. Goulard's extract produces a deep precipitate, and the supernatant liquor becomes colourless.

The watery solution when long exposed to the air becomes mouldy, and then gives an abundant precipitate with gall-nut, but when



the solution is recent this reagent only slightly disturbs it.

Spirit of wine dissolves aloes with great ease when warm. The solution is of a very deep red, and water added to it gives a copious pale yellow sediment. If the spirituous solution is much lessened by evaporation, the slightest agitation causes the surface to assume a crystalline form.

Neither the fixed nor the essential oils dissolve any sensible portion of aloes.

All the alkalies dissolve aloes very easily even without heat, and the intense bitter is somewhat corrected in this solution.

The ammoniacal solution carefully evaporated almost to dryness, gave the author a number of needled crystals impacted in a resiniform mass. These crystals gave the smell of ammonia when rubbed with lime and moistened, and hence this alkali appears to be one of their component parts.

Weak acids merely dissolve aloes, and somewhat more abundantly than water does.

Nitric acid dissolves it easily in the cold, producing a blood-red liquid, precipitable by water. A quantity of aloes was put into a retort and heated cautiously with eight parts of strong nitric acid. Abundance of nitrous gas was given out, and when this action had ceased the retort contained a yellow liquid, which on cooling deposited a good deal of a yellow flocculent substance, that weighed after washing on the filter about a quarter of the weight of the aloes employed. The author considers this as an acid possessing some peculiar properties, and terms it the *Aloetic Acid*. It is of a very fine yellow and intensely bitter, not crystallizable, reddens litmus, and effervesces with the alkaline carbonates. Its smell is agreeably aromatic when warmed. It is very slightly soluble in water, and the solution has the colour of arterial blood. Alcohol dissolves only  $\frac{3}{10}$  of its weight of this acid. The mineral acids merely dissolve without decomposing it. Potash forms a red crystallizable salt with this acid, which detonates with the violence of gunpowder when heated sufficiently or touched with an ignited body. The salt is easily produced by pouring a weak solution of caustic potash on the yellow aloetic acid.

The liquor that remains after the extraction of this acid from the heated mixture of aloes and nitric acid, contains also much oxalic acid, so as to give a copious precipitate of oxalate of lime on the addition of nitrat of lime.

\* An. Ch. tom. 68.

M. Braconnot infers from his experiments, that the chief constituent part of aloes is neither a gum nor resin, but a substance *sui generis*, which he terms *Bitter Resin* (*Resino-Amer.*)

M. Trommsdorff has given a comparative analysis of the Socotrine and Hepatic aloes,<sup>d</sup> of which a few particulars may be mentioned. Four ounces of aloes were boiled with 3 pints of distilled water. The whole dissolved, but became very turbid on cooling, and a yellow substance separated, weighing an ounce after drying. This substance was a bitter, yellow, brittle, transparent resin, fusible at a gentle heat, insoluble in water, very soluble in alcohol and potash, and highly inflammable.

The liquor that contained that part of the aloes which remained soluble in water, was evaporated to dryness, and gave a brown bitter mass equally soluble in water and alcohol, but insoluble in ether, which the author considers as identical with what Hermbstaedt terms the *Saponaceous Principle* of vegetables. Another portion of aloes was analyzed by first digesting it in alcohol, in which it totally dissolved without any residue but a few grains of woody impurity. The solution remained clear after cooling. After being evaporated to dryness, the residue was digested with water, and only three fourths of it dissolved, leaving one fourth of resin; which confirmed the general proportion of resin and other matter found in the first experiment.

Some difference was found in the subsequent analysis of the *Hepatic* aloes, this species containing about  $\frac{1}{10}$ th of albumen which resisted solution in boiling water and in alcohol, owing to its coagulation. This therefore is given as a mode of distinguishing the two species; the Socotrine aloes dissolves entirely in boiling water and in alcohol, but the Hepatic when thus treated, leaves a portion of coagulated albumen.

Further experiments have been made upon aloes by Messrs. B. La Grange and Vogel,<sup>e</sup> with some slight difference as to results.

A portion of each kind of aloes was distilled *per se*. Some water and oil passed over, the former of which gave a brownish-black colour to sulphate of iron, but this tinge did not resemble that produced by the distilled water of the gall nut; neither was the water of the aloes at all altered in colour by lime, barytic or strontian-water, all of which give a blue, green, or rose-colour precipitate with these

<sup>e</sup> An. Ch. tom. 68.

reagents. Hence the authors conclude that aloes contains no gallic acid. The distilled water of the hepatic aloes gave a sensible quantity of ammonia.

A second distillation of each species of aloes was made with the addition of water in the retort. The socotrine aloes gave a pleasant sweet-smelling water, not acid, on which floated a greenish yellow oil smelling like melilot. The distilled water of the hepatic aloes on the other hand was nauseous, and no oil separated.

The action of cold water on aloes was somewhat different from that observed by M. Braconnot. The latter chemist asserts that cold water in sufficient quantity will dissolve the whole of the aloes, and that the last dissolved portion equals the first in bitterness. On the other hand, the authors of the present paper found that by digesting the aloes with successive portions of cold water, and pouring off the liquors after remaining for some hours in contact till nothing more was extracted, there remained a soft grey elastic mass insoluble in water, resembling a resin. The watery solution is thick and lathers much on agitation. It deposits a yellow powder on the addition of a great variety of substances, such as all the mineral acids, all the neutral, and a great many of the metallic salts. Those of iron produce a brown precipitate, but different from that given by galls. All these precipitates from the aloetic solution are soluble in water. The watery solution, evaporated slowly to dryness, leaves a brown transparent vitriform mass intensely bitter, and perfectly soluble in water and alcohol, but very sparingly in ether.

On the other hand the resinous matter of aloes is not soluble in cold water, but dissolves in alcohol and ether, and the latter solution is abundantly precipitated by water.

The action of nitric acid observed by these chemists was nearly the same as that described by M. Braconnot. The yellow powder produced by heating aloes in this acid, gives a most beautiful purple colour to a large quantity of water. When this powder is gently heated *per se* in a retort, as soon as it melts, it explodes slightly, and an acid yellow bitter liquor passes into the receiver, smelling of prussic acid and evolving ammonia on the addition of potash.

Oxymuriatic acid passed through a concentrated watery solution of aloes is absorbed in great quantity, the liquor becomes yellow and coagulates strongly so as almost entirely to solidify. This coagulum when washed is elastic,

insoluble in cold water, but abundantly soluble in alcohol, which solution is copiously precipitated by water. The action of oxymuriatic acid therefore appears to convert much of the aloes into a perfect resin.

#### ALUM.

##### § I. *Ores and Manufacture of.*

The largest alum mine in Britain is at Hurlitt near Glasgow.<sup>a</sup> In the colliery at that place is a bed of coal about five feet thick covered by a roof of pyritical slaty clay of the thickness of ten inches. The coal with the superincumbent roof dips just enough to afford a free passage for the water, and the mine is worked, contrary to the usual practice, from the rise to the dip; hence all the workings are necessarily kept perfectly dry. For three centuries has this colliery been in work, and it now presents an excavation the area of which is nearly a mile square, with pillars of coal at the usual intervals in order to support the overlying beds, the thickness of which is on an average about 30 fathoms. The air circulates slowly through the whole of this space by means of such of the old shafts as still remain open; and, in consequence, a slow decomposition of the roof is perpetually going on. This process however is so gradual that in no part has the slate been hitherto entirely removed.

The first action of the air is to cause a thin flake to scale off from the roof and fall upon the dry floor; in this last situation the decomposition makes further progress, and by degrees assumes the appearance of a light spicular efflorescence. Succeeding flakes go through a similar process, and in time the whole space up to the very roof itself is completely filled; the current of air being then obstructed, all further decomposition of course ceases till the effloresced portion is removed.

The mass thus obtained consists of earth richly impregnated with sulphate of alumine, sulphate of iron, and in some cases with sulphate of magnesia. The salts are separated by lixiviation from the insoluble residue, the sulphate of alumine is converted into alum by the addition of sulphate or muriate of potash, and the manufacture is finished in the usual way.

The oldest alum works in this country are at Whitby in Yorkshire,<sup>b</sup> where there occurs a vast deposit of alum slate about twenty-nine miles broad from N. to S. and stretching from the eastern coast even into Lancashire. The depth of this mass is unknown, but it is covered

<sup>a</sup> Ph. Journ. xvi. p. 233.

<sup>b</sup> Ph. Journ. xxv. p. 241.

by alluvial soil, by sandstone lying upon or sometimes inclosing a thin bed of coal, by ironstone, shale and clay.

The alum slate itself, although tender near the surface, is at the depth of about 100 feet equal in hardness and compactness to common roof-slate. The upper part, whether from being actually richer in pyrites, or in a state of partial decomposition, is found to yield four or five times as much alum as the lower part, this latter being at the same time considerably more bituminous. Ammonites, nautilites, and trochites, together with belemnites, abound in the schistus; vertebræ and other bones of amphibious animals are also met with. Wood converted by bituminization into a more or less perfect jet is of not unfrequent occurrence, and several subordinate beds of red iron ore are worked at the depth of about 200 feet.

The alum slate being procured by means of the pickaxe, the first process to which it is subjected is roasting. For this purpose a bed of faggots and brushwood four or five yards broad and two yards high is covered to the height of about four feet with the ore broken very small; it is then kindled, and fresh ore is continually added; the breadth of the pile is also increased by successive additions of faggots and ore till at length the mass reaches the height of 80 or 100 feet, covering an area 150 or 200 feet square, and containing about 100,000 cubic yards of ore. The combustion is moderated by covering the surface with the more earthy part of the ore, and after a time it is extinguished spontaneously.

Of this calcined mine it takes on an average 130 tons to produce one ton of alum. For this purpose the ore is steeped in pits containing about 60 cubic yards at a time, and the solution (technically called alum liquor) is drawn off into a cistern, from which it is again pumped upon fresh calcined mine. This process is repeated till the liquor acquires a specific gravity of 1.15. The ore after having been once steeped is lixiviated again a second and third time, and these weaker solutions are used instead of water in subsequent steepings.

The strong liquor is drawn off into cisterns where it deposits much selenite and oxyd of iron; it is then boiled for a short time and allowed to cool, by which nearly the whole of the grosser impurities are got rid of. The liquor thus clarified is transferred to a leaden boiler, where it is mixed with a quantity of mother liquor and kept briskly boiling during the whole

day, the loss from evaporation being from time to time supplied by fresh liquor. The concentrated solution from the whole of the pans is run every morning into a vessel called a settler, where its specific gravity is taken, and is generally found to vary between 1.45 and 1.5: a solution of crystallized muriate of potash is then added, sufficient to lower the specific gravity to 1.55, and the whole is carefully mixed together. The liquor then stands in the settler about two hours in order to deposit the sediment which it contains, and when clear is transferred into the coolers to crystallize. After standing four days the mother liquor is drained off, and the crystals of alum washed with water in a tub, whence they are conveyed to a bin with holes in the bottom that the moisture may run off. The washed alum is then put into a large leaden pan with as much water as is requisite to hold the salt in solution at a boiling heat; the solution being complete the hot liquor is immediately run into casks. Here it remains about sixteen days; at the end of which time the casks are taken to pieces in order to get out the hollow mass of alum entire; this latter is then pierced, the mother liquor is let out and the alum itself being cleared from any adhering dirt is broken into pieces of about 1 cwt. each, and is ready for sale.

130 tons of calcined mine afford 1 ton of alum.

The daily produce of each pan is about 4 cwt. of alum, for which about 18 bushels of coal are required.

22 tons of muriate of potash are necessary for every 100 tons of alum.

#### § 2. Analysis of Alum.

The most accurate analysis of alum is by Vauquelin<sup>a</sup>; in his comparative examination of several varieties of this salt, for the purpose of ascertaining whether there is any such real superiority of the Roman alum, and of certain other foreign varieties of the same substance, over the French manufactures of this article as it seems, is generally supposed by the French dyers and calico-printers. The four most interesting varieties out of the six which were analysed by this able chemist, were the following: 1. Genuine Roman alum. 2. Ditto from a manufacture at Liege. 3. Ditto English. 4. Ditto French from the manufacture of M. Ribaucourt.

The method pursued was to dissolve the alum in water, and by the addition of ammonia in excess to separate the alumine and oxide of iron, the precipitate being perfectly well

<sup>a</sup> Ann. Chim. l. p. 154.

washed was dried and finally ignited in a platina crucible. A fresh portion of alum was then taken and decomposed by muriatic acid for the purpose of ascertaining the amount of sulphuric acid from the sulphate of barytes produced. The ammoniacal liquor in the first process was evaporated to dryness, the residual salt was ignited in order to drive off the sulphate of ammonia, and the remainder was sulphate of potash. A fresh portion was boiled in a retort with caustic potash, and the ammoniacal liquor which came over was saturated

with sulphuric acid and then evaporated; the remaining sulphate of ammonia indicated the amount of volatile alkali contained in the alum. Lastly, the alumine obtained in the first process was digested in caustic potash till the whole of the earth was taken up, and thus separated from the oxide of iron which is insoluble in this menstruum. From analyses carried on in the manner just mentioned it appears that the following are the component parts of the four varieties of alum examined by M. Vauquelin, viz.

Roman	—	Liege	—	English	—	French	
10.96	—	10.39	—	10.21	—	10.16	Alumine
31.82	—	31.49	—	31.64	—	31.49	Sulphuric acid
12.17	—	12.17	—	12.20	—	12.45	Potash
0.	—	0.29	—	0.47	—	0.41	Ammonia
0.	—	0.098	—	0.246	—	0.262	Oxyde of Iron
<hr/>		<hr/>		<hr/>		<hr/>	
54.35	—	54.438	—	54.766	—	54.772	

What remains to be added to each, that the original 100 parts may be complete, is water of crystallization.

Hence it appears that the sole difference between the most and the least valued kinds of alum is that the latter contains a few thousandths of the sulphates of ammonia and of iron, which are wholly or almost wholly wanting in the former. It became therefore a matter of importance to ascertain by direct experiment the effect of a small portion of these salts upon the more delicate dyes, and in consequence an investigation to this purpose was undertaken by M. M. Thenard and Roard.<sup>a</sup>

The result of their inquiry has been, that in dyeing *wool* with the most delicate colours, such as weld, cochineal, sumach, madder and kermes, the use of Roman instead of common alum is of little or no consequence; that the colours of *cotton* are sensibly deteriorated by the employment of impure alum, and that this effect is still more sensible in the dyeing of *silk*. Sulphate of ammonia even in much larger doses than it exists in the most impure alums is very little injurious, it is therefore the sulphate of iron that produces all the mischief.

Having thus ascertained that the preference given to the Roman over every other kind of alum in the market is by no means a prejudice, but founded on very substantial reasons, M. M. Thenard and Roard proceed to show that it is very easy to get rid of the sulphate of iron, and thus to raise the most impure alums completely to the standard of the Roman. For this purpose the alum is to be dissolved in as small a

quantity as possible of boiling water, and the solution while cooling is to be incessantly stirred; by this means the alum will be obtained nearly in a pulverulent state; it is then to be carefully washed two or three times in small portions of fresh water, and the purification is complete. [For the experiments of Thenard and Roard on the action of alum on colouring matter, see the article *DYING* in this Appendix.]

#### ALUMINUM.

The metallic basis of alumine has not yet been obtained in a free state, though sufficient indications of its existence have been made out by Sir H. Davy.<sup>a</sup> When iron is negatively electrified with a high galvanic power and fused in contact with moistened alumine, a globule is obtained whiter than pure iron, which slowly effervesces in water and becomes gradually covered with white powder; and the solution in muriatic acid decomposed by an alkali gives alumine and oxyd of iron. Also when potassium is vaporized by heat, and in this state passed through alumine heated to whiteness, much potash is formed which produces a coherent mass with the undecomposed alumine, in which are found numerous grey particles which become white when heated in the air, and slowly effervesce in water. These grey particles appear to be an alloy of potassium and aluminum.

#### AMMONIA. AMMONIUM.

The following practical remarks on the preparation of the liquid ammonia may be

<sup>a</sup> Ann. Chim. lix, p. 58.

<sup>a</sup> Elements of Chemistry.

useful. Mr. Phillips has the following experiment.<sup>a</sup> To 9 oz. of lime slacked with half a pint of water, and put in a closed vessel, were added 12 oz. of muriat of ammonia, and 3  $\frac{1}{2}$  pints of boiling water. The mixture having cooled, the clear solution was divided into two equal portions and separately distilled, without putting any water in the receiver or employing pressure. Ten ounce measures of distilled liquor of ammonia were obtained from each portion, of the specific gravity of .954, which according to Davy's tables indicates about 11  $\frac{1}{2}$  per cent. in weight of the pure alkali. The quantity of lime here used is amply sufficient, indeed the same weight as the muriat of ammonia would be sufficient, if the lime is made from marble or any pure limestone, and thoroughly well burnt.

Mr. Dalton<sup>b</sup> has given a table of the strength of ammoniacal solutions somewhat differing from that of Davy. The data which Mr. Dalton assumes, (from particulars which need not be here enlarged upon) and on which the accuracy of the table depends, are the following:

100. water-grain measures of liquid muriatic acid of 1.074 sp. gr. contain 11. grains of real acid: the specific gravities of muriatic acid gas and ammoniacal gas are in the respective proportions of 1.23 and 0.6 and 11. measures of the acid gas saturated 12. measures of the ammoniacal gas. No allowance is required for condensation in constructing the following table, it having been found both by Davy and Mr. Dalton, that when liquid ammonia is mixed with water, the specific gravity is as nearly as possible the mean of the two. Mr. Dalton's table is the following.

Specific gravity.	Grains of ammonia in 100 water-grain measures of liquid.	Grains of ammonia in 100 grains of the liquid.
.85	30.	35.3
.86	28.	32.6
.87	26.	29.9
.88	24.	27.3
.89	22.	24.7
.90	20.	22.2
.91	18.	19.8
.92	16.	17.4
.93	14.	15.1
.94	12.	12.8
.95	10.	10.5
.96	8.	8.3
.97	6.	6.2
.98	4.	4.1
.99	2.	2.0

<sup>a</sup> Examinat. of the Pharm. Lond. 1811. vol. III.

<sup>b</sup> New System of Chemical Philosophy, vol. 2d.

<sup>c</sup> Philos. Trans. for 1809.

#### Analysis of Ammonia.

In the article *Ammonia* (Chem. Dict.) we mentioned the experiments of Priestley, Berthollet, and other chemists, which shewed this alkali to consist of azote and hydrogen, in the proportions of about 4 parts by weight of the former, and 1 part of the latter. A number of important researches have since been made by several eminent chemists, which require a detailed notice.

The fixed alkalies being proved by Davy to be compounds of a peculiar metallic base and oxygen, it naturally occurred to this eminent philosopher that the analogy with the other alkalies would infer a similar composition in the volatile alkali, which however seemed to be contradicted by the experiments of Berthollet and Sir H. Davy himself, in which ammonia was wholly resolved into azote and hydrogen, unless either of these latter substances was itself an oxyd of some unknown base.

A very laborious series of experiments on the analysis of ammonia by electricity and combustion with oxygen and other gasses, has been published by Dr. Henry,<sup>c</sup> which we shall detail somewhat at large, on account of the great importance of the subject, the admirable practical skill and ingenuity with which the experiments were carried on, and the clear idea which it gives of the extreme difficulty which exists in obtaining perfectly accurate results in these delicate operations, from a variety of causes that are here explained.

The first object is the apparatus. Dr. H. found in former experiments that in the usual way of electrizing gasses, a temporary communication is made with the atmosphere at the moment of the explosion, which in the course of a long experiment is sufficient to introduce so much atmospherical air, as sensibly to affect the result. The only unobjectionable way, as Dr. H. mentions, is to inclose and hermetically seal the explosion wires in glass tubes, and then to grind away so much of the glass as will expose the ends of the wires. Those employed in these experiments were of platina,  $\frac{1}{50}$  of an inch in diameter.

The next and most difficult object is to free the ammoniacal gas entirely from water. The avidity with which this gas retains moisture is very remarkable. A confined quantity of common air may be so completely desiccated in a few minutes by pure dry potash or dry muriat of lime, that no ice shall appear on the

surface of the vessel when exposed to a cold of  $-26^{\circ}$ . But ammonia requires exposure during some hours to potash to stand the test even of the temperature of 0. and a single transfer of the dried gas through mercury in ordinary use, again communicates moisture to it. The gas employed in these experiments was dried by sticks of pure potash fastened to steel wire, so that they could be withdrawn through the confining mercury when their drying action had ceased, and this was ascertained by applying ether or salt and snow to the outside of the glass. In some of the first experiments Dr. H. found that though the gas thus prepared deposited no moisture by cold before electrization, yet it gave a sensible quantity afterwards; but on applying heat just before the experiment both to the mercury and the iron cistern containing it, this condensation of moisture after electrization no longer appeared; at least only in the slightest possible degree; so that it seems necessary for perfect accuracy to heat the mercury and vessels as well as to dry the gas, and even to boil the mercury in the tube before admitting the ammonia.

With these precautions given quantities of ammonia were subjected to long continued electrization, by which (as already mentioned in our former article) the bulk of the gas is nearly doubled, and when no further increase takes place, the residue has now lost its alkaline properties, and is entirely resolvable into azote and hydrogen. Dr. Henry found from the mean of six experiments that 100 measures of pure ammoniacal gas were resolved by electricity into 198.78 measures of the mixed gasses, but the results of the experiment on which he placed the most confidence, on account of the scrupulous precautions observed against the intrusion of moisture, gave an increase of only 180.6 from 100 of ammonia.

The proportion of the hydrogen and azote to each other was ascertained by passing into the mixture a known quantity of oxygen gas, firing it with the electric spark, and estimating the hydrogen thus consumed, the azote being unaltered and constituting the chief part of the residue. In making this estimation, two measures of hydrogen are reckoned as saturating one measure of oxygen for the composition of water. Even this part of the experiment is liable to some inaccuracy as Dr. H. observes, for it is necessary to use a redundance of oxygen gas to explode the whole of the hydrogen, but it is by no means certain that a small portion of the azote will not also undergo combustion

into nitric acid which will be absorbed by the water generated. On the whole, Dr. Henry estimates the entire mixed gasses produced by the electrization of the ammonia, to be composed of about 74 measures of hydrogen to 26 of azote.

The extreme labour of decomposing ammonia by mere electricity, led the author to attempt a shorter mode of analysis. Ammonia and atmospherical air will not explode by the electric spark in any proportions, but Dr. H. found that ammonia and oxygen gas when mingled in proper proportions, may be detonated over mercury by the electric spark with as much ease as a mixture of hydrogen and oxygen, and this experiment affords a very ready way of analyzing ammonia with infinitely less labour than by simple electrization, and with as much accuracy, provided proper precautions are observed.

With a greater proportion of pure oxygen gas to ammonia than that of three to one, or of ammonia to oxygen than that of three to 1.4 the mixture ceases to be combustible, but when the proportions best adapted to inflammation are used, the oxygen may be diluted with six times its bulk of common air, without losing its property of burning ammonia.

The products of the combustion of ammonia with oxygen vary essentially, according to the proportion of the gasses used. If the oxygen gas be as much as double the ammonia, the ammonia entirely disappears, as well as the hydrogen, and the only residue is azote with the excess of oxygen. The moment after the detonation, a white cloud settles on the inner surface of the tube, which is too small for analysis but is probably nitrat of ammonia, the nitric acid being formed by the oxygenation of a portion of the azote. Hence when the oxygen of the residue is removed by sulphuret of lime or any other eudiometrical process, the quantity of azote remaining is less than ought to be produced from the ammonia decomposed.

On the other hand when less oxygen is added at first to the ammonia than is sufficient to saturate all the hydrogen, that is to say, when the ammonia much exceeds the oxygen, no nitrat of ammonia appears, the mixture being free from cloudiness, and the mixed gas remaining after the first detonation will completely lose its hydrogen by a second admixture with oxygen and firing, and the azote will remain untouched.

Dr. Henry gives the results of comparative experiments in the two cases, that is, where an excess of oxygen was first employed; and where a deficiency was used. In the first case the oxy-

gen used was twice the measure of the ammonia: the whole was decomposed by a single explosion; and the hydrogen being estimated as equal to twice the bulk of the oxygen that disappeared, and the residuary azote being measured after the removal of the remaining oxygen by sulphuret of lime, the composition of 100 measures of ammonia was estimated to be 84.29 hydrogen, and 15.71 azote, numbers far remote from those given by all the other modes of analysis.

On the other hand, when the ammonia was fired with a deficiency of oxygen gas, 63 measures of the former were exploded with 33 of oxygen holding 1. of azotic impurity. These were diminished to 57 by the first explosion, and no part of the residue was absorbable either by water or by sulphuret of lime, shewing that the whole of the ammonia was decomposed, and that all the oxygen employed had been consumed. The remaining 57. measures (consisting of hydrogen and azote) were detonated with a further addition of 40. of oxygen, and the residue after this second detonation amounted to 60, which was further analyzed by sulphuret of lime. By calculating as above, reckoning 2 measures of hydrogen for every measure of oxygen actually consumed, it appears that the original 63 measures of ammonia furnished by decomposition 31.34 of azote and 88.66 of hydrogen, and hence 100. measures of ammonia would furnish 73.88 of hydrogen to 26.12 of azote.

Dr. Henry gives the results of six experiments on the decomposition of ammonia with a deficient proportion of oxygen, but we must confess that though they attest the care and fidelity of the experimenter, there is not quite sufficient agreement between them to lead us to place implicit confidence in this mode of operating, even in the most skilful and practised hands. The proportion of permanent gasses to the ammonia decomposed, (the azote being actually measured, and the hydrogen estimated by doubling the oxygen expended) varies not inconsiderably in the six experiments, the highest being 198 $\frac{1}{2}$ , the lowest 180.2 from 100 of ammonia. This shews a correspondent variation of from 66 to 72.2 of oxygen required to saturate all the hydrogen of 100. measures of ammonia, a variation which, however, is probably not more than may be expected in the best conducted experiments on such a complicated subject that requires such a variety of precautions to ensure a tolerable uniformity.

The author ascribes these variations chiefly to the great difficulty of expelling all adhering

moisture from every part of the materials and apparatus employed, and his general result is that the proportion of oxygen most precisely necessary to saturate 100. measures of ammonia is 67 $\frac{1}{2}$ , (or 100. of oxygen to 148 of ammonia) and the 100 measures of ammonia will afford about 136 measures of hydrogen and 47 of azote.

Dr. Henry also finds that ammonia will explode with nitrous oxyd and with nitrous gas.

A series of experiments on the decomposition of ammonia has also been published by Mr. A. B. Berthollet,<sup>d</sup> the principal object of them was to examine a position laid down by Davy, (which we shall presently notice) that ammonia contains about  $\frac{1}{11}$  of its weight of oxygen. M. A. B. Berthollet relates several experiments relative to the de-oxydation of iron in ammoniacal gas, and the decomposition of ammonia by its passage through an incandescent tube; and by electricity. In the latter method he gives as the mean of six experiments, that 1. measure of ammoniacal gas dilates by electrization into 2.04643 measures of hydrogen and azote.

His general results are that 1 litre of ammoniacal gas is decomposed into 2.046 litres of mixed gas, of which 1.545 is hydrogen, and 0.146 is azote. The weight of this quantity of hydrogen is 0.146 grammes, and that of the azote is 0.630 grammes, amounting in the whole to 0.776; and the weight of a litre of ammonia is 0.775 grammes, which agrees so nearly with the former as to demonstrate (if the data be correct) that ammonia contains no oxygen, nor other constituent part besides hydrogen and azote. It must be observed, however, that the experiments of this ingenious chemist (now no more) do not appear to have been conducted with the same scrupulous attention as those of Dr. Henry. In particular, the means used for depriving the gas of moisture were not so carefully attended to; and in the analysis by combustion with oxygen, an excess of this latter gas was used, which produced so much nitric acid as sensibly to redden litmus, and thus to embarrass the results. The presence of moisture will account for the greater expansion by electrization which this chemist gives; for Dr. Henry uniformly found, when the ammonia was at the driest, that the expansion never quite doubled the original volume of the ammonia.

Mr. Dalton agrees with Sir H. Davy and Dr. Henry, that the volume of ammonia is not doubled by decomposition, but that 100. measures of ammonia give from 185 to 190 of the mixed gasses, the respective proportions of

<sup>d</sup> Mem. d'Arcueil, tom. 2.

which are about 28 measures of azote gas to 72 measures of hydrogen in the hundred.

100 measures of ammonia at .6 sp. gr. weigh 60 grains.

These become by decomposition 185. measures of mixed gas,  
 Namely 51.8 of azote which at .967 sp. gr. weigh 50.09  
 133.2 of hydrogen .08 10.65

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60.74

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Here the united weights of the hydrogen and azote equal and a little exceed the weight of the ammonia, and hence this alkali cannot contain any other constituent part than azote and hydrogen.

Mr. Dalton remarks on the analysis of ammonia by mixture with oxygen and detonation, that notwithstanding the elegance and expedition of Dr. Henry's method, it appears probable that a compound combustible such as ammonia is, can never be totally decomposed and one of its elements burnt, to the entire exclusion of the other. Thus in a mixture of carbonic oxyd and hydrogen, phosphorus, &c. where one of the elements seizes oxygen with more rapidity than the other, it is impracticable totally to oxygenate one of them, and leave the other untouched. With ammonia it is confessedly so where an excess of oxygen is used, (nitric acid appearing along with the water produced) and Mr. Dalton conceives that this is in some degree the case in whatever proportions they are fired. On the whole he prefers employing nitrous oxyd. When 100. measures of ammonia are exploded with 120. of nitrous oxyd, the gasses resulting are azote with only a very small portion of hydrogen. If to this a little hydrogen be added, and then an excess of oxygen, another explosion will determine the residuary hydrogen before explosion, which being deducted, there remain about 172 measures of azote, 120 of which come from the nitrous oxyd, and 52 from the ammonia, which gives after the rate of 28 per cent. of azote in volume on the evolved gasses.

We now proceed to the very interesting researches of Sir H. Davy on the nature of ammonia.

This eminent philosopher, after his most important discovery of the metallic bases of the fixed alkalies, was led from analogy to entertain the opinion that ammonia was probably, like the other alkalies, a compound of some peculiar metallic base and oxygen, and some experiments on the decomposition of ammonia, gave him reason to suppose that the hydrogen and azote evolved, were less than the entire weight of the

Mr. Dalton adds the following estimation.

alkali by about  $\frac{1}{11}$ , which eleventh part he concluded was the oxygen of the ammonia. This opinion, however, has been satisfactorily refuted by the laborious researches of Henry and Berthollet, just described; so that when ammonia is decomposed simply into hydrogen and azote, it appears that the united weights of these two elements equal the weight of the ammonia decomposed with as much accuracy as can be ever expected from such delicate experiments. This part of the controversy therefore seems to be put at rest, but another and highly curious set of phenomena happened to be discovered at the same time, which deserves particular notice.

Dr. Seebeck, of Jena, discovered in 1808, that when solid carbonat of ammonia is slightly moistened and placed in contact with mercury, and the whole connected with the Voltaic battery so that the mercury communicates with the negative pole and the salt with the positive pole, the mercury speedily becomes as soft as butter, expands in bulk, and has all the appearance of an *amalgam*. This when thrown into water effervesces strongly, the water becomes ammoniacal and the mercury returns to its original state. This experiment was repeated by Dr. Pontin and Professor Berzelius with some variation, and by them communicated to Sir H. Davy,\* who immediately pursued the subject with his accustomed skill and ingenuity. His principal experiments are the following: a cavity was made in a piece of muriat of ammonia, and into this a large globule of mercury was introduced. The muriat was slightly moistened and placed on a plate of platina, which was made positive in the circuit of the large battery. The quicksilver was made negative by means of a platina wire. A strong effervescence immediately took place, the globule in a few minutes enlarged to five times its former dimensions, and metallic crystallizations shot from it as a centre round the body of the salt, which, when accidentally broken off from the mass, rapidly disappeared, emitting ammoniacal fumes and reproducing mercury.

When a piece of moistened carbonat of am-

\* Phil. Trans. for 1808 and 1809.



monia was used, the appearances were the same, but a black matter formed in the cavity, apparently carbon.

It then occurred to Sir H. Davy that the strong deoxydating power of potassium or of sodium, might be made to produce the same effect on the ammoniacal salt without the intervention of any galvanic apparatus. Accordingly a small portion of potassium was dropped into the globule of mercury contained in the moistened cavity of the lump of muriat of ammonia, and immediately without any further apparatus, the mercury enlarged as before to six or seven times its bulk, and the same amalgam was formed, with this slight difference however, that it appeared to be more permanent, and to retain a portion of the potassium used.

This ammoniacal amalgam at the temperature of 70° or 80° is of the consistence of butter, at the freezing point it crystallizes into small undefined brilliant facets. When exposed to the air it soon becomes covered with a white crust of carbonat of ammonia. When thrown into water it produces about half its bulk of hydrogen, and returns to the state of running mercury, the water becoming ammoniacal. When thrown into muriatic acid gas, it instantly becomes coated with muriat of ammonia, and some hydrogen is disengaged. In sulphuric acid it becomes coated with sulphat of ammonia and sulphur.

The physical properties of this amalgam are very curious. The mercury appears to gain no more than about  $\frac{1}{1000}$ th of its weight of new matter, but is thereby rendered solid, has its specific gravity diminished from 13.5 to less than 3, and retains its metallic colour, lustre, opacity, and conducting power.

Sir H. Davy made many attempts to obtain a peculiar metallic substance from this amalgam, by distillation, out of the contact of air, and thus to exhibit the supposed basis of ammonia (or *Ammonium*), in a separate state. But all these attempts failed, for under every circumstance the amalgam, when heated, gave out hydrogen and ammonia, and the mercury returned to its former state. In the most accurate experiments the proportions of these two gasses evolved were two of ammonia and one of hydrogen.

The nature of this amalgam is still very obscure, and much difference of opinion prevails on this subject among chemists. As it seems well ascertained that ammonia is resolvable solely into azote and hydrogen, it fol-

lows, that if ammonia is really an oxyd of some metallic base, azote and hydrogen, or one of them, must also be oxyds of some hitherto unknown substance, and this idea has been adopted by M. Berzelius, in his elaborate analytical researches, who supposes both hydrogen and azote to be oxyds of ammonium in different proportions. But when the ammoniacal amalgam is distilled, hydrogen and ammonia both appear, and the source of the hydrogen remains to be accounted for. This Sir H. Davy does, by supposing that as the amalgam is formed from moist substances, sufficient water adheres to it to afford oxygen by its decomposition, whilst its hydrogen unites with the amalgam. Nevertheless an excess of hydrogen is always produced in the distillation of the amalgam, even where the most scrupulous care is taken to exclude moisture.

Before we proceed with the other decompositions of ammonia, we shall relate the experiments of Messrs. Gay Lussac and Thenard,<sup>f</sup> on the ammoniacal amalgam, in which they have repeated the experiments of Seebeck and Davy, and have added other interesting facts. They observe that when the amalgam is formed by the agency of galvanic electricity upon mercury in contact with moistened muriated ammonia, the acid of the salt and the oxygen of the water are carried to the positive pole, round which a dense and suffocating vapour of oxymuriatic acid collects. On the other hand, little or no gas of any kind escapes at the negative pole; but if the mercury is removed, then the effervescence is equally great at this pole also; from which they infer that the mercury simply absorbs the gas that would otherwise have escaped, and forms the amalgam.

When this amalgam is well dried and inclosed in a dry bottle of common air, and simply shaken for a few minutes, it is entirely decomposed, running mercury is produced, and hydrogen and ammoniacal gas are found mixed with the air of the bottle, which is no way altered when examined by Volta's eudiometer. Hence it appears that this amalgam can only exist under the electric influence, and as soon as this is destroyed by agitation, it returns to its elementary state. The amalgam made in Davy's method by mercury, potassium, and muriat of ammonia, without the agency of electricity, is more permanent, and remains in this state as long as it contains any potassium, but as soon as this is destroyed the amalgam is suddenly broken up. A quantity of this amalgam

<sup>f</sup> Recherches Physico-Chimiques faites par M.M. Gay Lussac and Thenard.

was made, and the outer crust being removed by a knife, some of the inner part was taken up by a dry iron spoon, and put into a very dry glass tube inverted over mercury that had just been boiled. The tube being closed with a dry stopper was gently shaken, the amalgam was speedily decomposed, and a considerable quantity of gas was generated, consisting of ammonia and hydrogen in the proportion of about  $2\frac{1}{2}$  to 1. The authors say that it is impossible that any moisture should here be present, since this is incompatible with potassium, and hence it appears that the amalgam cannot contain any basis of ammonia (supposing the alkali itself to be an oxyd of some unknown basis) since there is no obvious source from which this basis could abstract oxygen when the ammonia is regenerated. The authors endeavoured to ascertain the respective quantities of ammonia and of hydrogen given out during the decomposition of the amalgam, and they found that the mercury of the amalgam gave about 3.47 times its volume of hydrogen, and 4.22 of ammonia, which together made  $\frac{107000}{100000}$  of the weight of the mercury.

*On the action of Potassium on Ammonia.*

When potassium is fused in ammoniacal gas,<sup>§</sup> it is gradually changed into a very fusible olive-green substance, the ammonia disappears entirely, and part of the space which it occupied is filled with a quantity of hydrogen exactly equal to that which the potassium employed would have given, if thrown into water. This experiment may be performed in a bent tube over mercury, but care must be taken to shake off every particle of mercury from the potassium before it is deposited in the bend of the tube. Heat is then applied by a spirit lamp, and soon the potassium melts and becomes covered with a thin crust which directly after disappears, leaving the surface very brilliant, in a few seconds much ammonia is absorbed, and the olive-green substance is produced. By using sufficient ammonia all the potassium is changed to this olive-green matter. The quantity of ammonia absorbed varies from less than 100 to 156 times the bulk of the potassium, according to the heat employed. This olive-green substance is opaque, and heavier than water, when heated it melts and disengages ammonia, hydrogen, and azote, and then solidifies, still retaining its green colour. When exposed to the air at a common temperature, it gradually changes to ammonia and potash. When thrown into a heated crucible it suddenly

inflames. It burns rapidly when heated in oxygen gas. In water it heats and is immediately decomposed into potash and ammonia. The same effect takes place with acids. When heated with most of the metals, particularly the easily fusible ones, azote, ammonia, and sometimes hydrogen are disengaged, and an alloy of potassium with the metal used is obtained. M. M. Gay Lussac and Thenard examined with much care the effects produced by the application of different degrees of heat to this olive-green matter. The potassium was first put into a glass vessel with a certain quantity of pure hydrogen, to preserve the potassium from the contact of the mercury by which it was confined. Some pure ammoniacal gas was then added, and the whole was heated till the olive-green matter was produced, and when cold the absorption of ammonia was ascertained. The olive-green matter was then heated gradually to redness in the same vessel, without being removed, when it melted, boiled, and finally became solid again, blackish, and was no longer fusible. The remaining ammonia was then absorbed by water, and the azote and hydrogen analyzed in Volta's eudiometer. The general results of several experiments at different degrees of heat was, that as soon as the heat is sufficient to melt the olive-green matter, it begins to give out gas; that as long as the heat does not quite reach a cherry red, the gas is only ammonia; but by raising the heat to low redness, much hydrogen and azote become mixed with the ammonia given out; and at a higher heat, the gas becomes entirely hydrogen and azote, in the proportions of three to one, that is, in which they constitute ammonia; but however long the heat is continued, no more than about three-fifths of the quantity of gas originally absorbed by the potassium is expelled, so that it does not return to the state of potassium, but to a blackish infusible compound.

When this olive-green matter is confined over mercury and a drop of water is let up to it, much heat is excited, and a good deal of gas generated. By carefully adding water as long as any gas is generated, and assisting the process by a gentle heat, the whole is converted into a lump of moist solid potash and pure ammoniacal gas; and it was found that the ammonia obtained was almost equal to that which had been originally absorbed by the potassium, during its conversion into the olive-green matter, the slight difference in quantity

<sup>§</sup> Recherches Physico-Chimiques, faites par M. M. Gay Lussac and Thenard.

being attributed to the ammonia absorbed by the moistened potash.

Sir H. Davy has also made a number of experiments on this singular compound with results some of which agree with those of Messrs. Gay Lussac and Thenard, and others differ from them. Some of these we shall mention,<sup>b</sup> particularly the properties of the residuum of the olive-green substance after it has been heated to redness.

Its colour is black and in lustre it resembles plumbago. It is opaque, and brittle. It is a conductor of electricity. It does not fuse at a low red heat, but gives out a dark coloured sublimate. When exposed to the air at a common temperature it usually takes fire immediately and burns with a deep red light. When it is acted upon by water it heats, effervesces violently, and is resolved into ammonia and potash, with a little inflammable gas. It has no action upon quicksilver. It combines with sulphur and phosphorus by heat, and these compounds when wetted inflame and give out, the one sulphuretted, and the other phosphuretted hydrogen gas.

On distilling this substance in a tube of wrought platina in a very intense heat, potash was found with a quantity of potassium in the tube, and the gas was hydrogen with only a small proportion of azote.

The remarkable circumstance of this experiment is the deficiency of azote, this substance being in much less proportion than is required to constitute ammonia if the analysis of this alkali by electricity be at all correct.

After all that has been done on the analysis of ammonia, no satisfactory proof has yet been given that it can be decomposed into any other elements than azote and hydrogen.

#### AMMONIAC. (GUM.)

This gum has been examined by M. Braconnot.<sup>a</sup> Exposed to a very gentle heat it loses 6 per cent. of its weight of mere moisture. Distilled *per se*, it yields half its weight of a brown empyreumatic oil containing ammonia. The coal contains phosphat and carbonat of lime.

Twenty five grammes of gum ammoniac were boiled with alcohol. The whole was dissolved except 5.8 grammes, and the solution remained clear on cooling. The insoluble portion was heated with water and the greater part dissolved, leaving however a grey glutinous mass insoluble both in water and spirit of wine.

The watery solution left a gum on evaporation, which was transparent, reddish yellow,

slightly bitter, and brittle: water easily dissolves it. It is abundantly precipitated by Goulard's extract, (but *not* by the acetite of lead) and only very partially by the nitrats of mercury and of lead. Lime water does not alter the solution, but oxalat of ammonia separates some oxalat of lime.

The resin produced by the evaporation of the alcoholic solution of gum ammonia is reddish yellow, transparent, brittle, but easily softens between the fingers. It has no taste. It unites with the alkalies with ease, even without heating, and the result is a saponaceous bitter solution.

Sulphuric acid dissolves the resin quietly in the cold, and the solution is separated by water.

When nitric acid is heated on this resin, it is suddenly decomposed with much red vapour. On evaporating the liquor to dryness a bitter resin is obtained which melts at a low heat, unites to alkalies, dissolves in alcohol and in water, and precipitates in part from the latter if it has been used boiling. Cold water also dissolves much of this bitter resin, giving a very beautiful yellow colour that stains the fingers strongly, and fixes itself easily and most firmly to silk and wool, so as to become unalterable by oxymuriatic acid, and even by alkalies if weak.

Gum ammoniac contains 18.4 per cent. of gum; 70. of resin; 4.4 of matter resembling gluten; and 6 of moisture.

#### AMPHIBOLE.

At the end of the article of STRAHLSTEIN it is remarked that a strong analogy subsists between the several varieties of Hornblende, Actynolite, Tremolite, and Asbestos. M. Haüy has since, in his *Tableau comparatif*, entered into an interesting discussion of this question, and from crystallographical resemblances, aided by the results of recent chemical analysis, has arranged them in the following manner.

The Labrador Hornblende forms a species by itself, under the name HYPERSTENE. The resplendent Hornblende (Schillerspath or Bronzite) forms a variety of DYALLAGE, the *metalloide*. A few of the Strahlsteins constitute the species EPIDOTE, (Thallite of Karsten) the remainder of the Hornblendes and Strahlstein, and all the Tremolites are included under the species Amphibole. Asbestos for the present ranks as a distinct species, but M. Haüy cites with evident favour the opinion of Cordier, who is for including it under Amphibole.

The following are the essential crystallographical characters of amphibole. Its primitive crystalline form is an oblique rhomboidal prism,

<sup>a</sup> Phil. Trans, for 1809.

<sup>a</sup> An. Chem. tom. 62.

the lateral planes of which unite under angles diagonally passing through the obtuse angles of alternately of  $124^{\circ} 34'$  and  $55^{\circ} 26'$ ; and the the summit is nearly as one to four. ratio between the height of the prism and the

The following are some of the most recent analyses.

Basaltic Hornbl. by Klappr.	Crystall H. from Cape de Gate, by Laugier.	Lamellar Hornbl. by Klappr.	Actynolite of Zillerthal, by Laugier.
47.	42.	42.	50. Silex
8.	9.8	11.	9.75 Lime
2.	10.9	0.	19.25 Magnesia
26.	7.69	12.	0.75 Alumine
15.	22.69	32.	11. Oxide of Iron
	1.15 Oxide of Manganese		5. Oxide of Chrome
<hr/> 98. <hr/>	<hr/> 94.23 <hr/>	<hr/> 97. <hr/>	<hr/> 95.75 <hr/>

Fibrans Tremolite, by Klappr.	Comm. Tr. by Lowitz.	Grey Tremolite, by Laugier.	Baikalite, by Lowitz.
65.	52.	50.	44. Silex
18.	20.	18.	20. Lime
10.33	12.	25.	30. Magnesia
0.16	0.	0.	6. Oxide of Iron
6.5		5.	Water and Carbonic acid
	12.		Carbonate of Lime
<hr/> 99.99 <hr/>	<hr/> 96. <hr/>	<hr/> 98. <hr/>	<hr/> 100 <hr/>

**ANALCIME.** Cubic Zeolite J. Wurfel Zeolith W.

It occurs limpid, or greyish-white; is amorphous, mammillated, radiated, or crystallized. Its form is a cube either perfect or with similar modifications round all the solid angles, producing symmetrical varieties that distinguish it from other species with which it might be confounded. It has rarely any natural joints visible, hence its fracture is compact conchoidal. It varies from translucent to transparent; usually scratches glass. sp. gr. 2.0.

Before the blowpipe it intumesces like borax and melts into a glass, emitting at the same time a phosphoric light. It is composed according to Vauquelin, of

58. Silex
18. Alumime
2. Lime
10. Soda
8.5 Water
<hr/> 96.5 <hr/>
3.5 Loss

**Var. I. Sarcolite**

Colour flesh red, opaque, somewhat softer than the preceding: consists, according to Vauquelin, of

50. Silex
20. Alumime
4.25 Lime
4.25 Soda
20. Water,
<hr/> 98.5 <hr/>
1.5 Loss

Analcime occurs chiefly in the glands of amygdaloid, and other trap rocks.

**ANALYSIS OF VEGETABLE AND ANIMAL MATTER.**

In an interesting memoir on this subject by Messrs. Gay Lussac and Thenard,<sup>a</sup> these chemists shew the great difficulties and the many causes of inaccuracy that attend the usual modes of analyzing vegetable and animal matter, and describe a new method of proceeding, by which they consider that they have been able to combine the carbon and hydrogen with the ut-

<sup>a</sup> Recherches, &c. tom. 2.

most quantity of oxygen with which they can unite, and thus by proper data to estimate the proportion of these constituent parts, and of oxygen, existing in the substance analyzed. The substance selected to oxygenate these elements is the oxymuriat of potash, and the matter to be analyzed is mixed with this salt and deflagrated in an apparatus contrived for the purpose, consisting of a thick glass tube set vertically in a fire with a lateral tube to conduct the generated gasses to a mercurial trough, and a cock above, the stopper of which is not perforated, but contains a small depression, into which a portion of the material to be analyzed is put, and by turning the cock downwards, this portion falls into the heated tube, and there deflagrates. The proportion of the oxymuriat requisite to burn completely the substance analyzed is found by previous trials in an open crucible, so much of the salt being required, that the residue after deflagration shall be quite white, or at least not carbonaceous; and in the actual experiment a considerable excess of the oxymuriat is employed. The materials are then accurately weighed (after being long dried at a boiling-water heat) and mixed in a mortar with a little water to an adhesive mass, which is divided by being thrust into a brass mould, and the pieces are rolled up by the fingers into little balls that they may drop clean from the stopper of the cock down into the deflagrating tube. These balls are again dried at the same heat before using.

The oxymuriat of potash is previously analyzed by itself in a proper apparatus to ascertain the proportion of oxygen which it furnishes, and to ensure an uniformity in this agent a considerable quantity of the salt is fused and then rubbed to powder by itself and kept for use. If the substance to be analyzed is a vegetable acid, it is combined with lime or barytes before mixture with the oxymuriat; and this calcareous or barytic salt is separately analyzed, and the carbonic acid that remains united with the earth after deflagration is properly estimated.

The earthy or other incombustible matter belonging to the substance to be examined is also separately estimated by calcining this substance by itself in a platina vessel and lixiviating the residue. The author gives at length all the precautions required in the management of the apparatus, both in preparing for the deflagration and in the estimation of the gasses produced. These last are supposed to be only carbonic acid, azote, and oxygen, the quantity of the oxymuriat being more than sufficient to convert into water all the hydrogen of the substance

analyzed. The probability of a little carburated hydrogen that may have escaped combustion is also acknowledged, and some allowance is made for it though apparently not in a very accurate way. The examination of the gaseous products of the deflagration is therefore thus conducted: 200 measures of the gas (standing over mercury) are added to 40 measures of pure hydrogen, and detonated by the electric spark. By this means the excess of oxygen is separated in the form of water, and the quantity of this excess is, of course, one third of the volume of the entire absorption after the electrization. The carbonic acid is absorbed by potash, and the residue is further examined for oxygen by the same means, and the ultimate residue is considered as azote. The data therefore from which the results of the analysis are made out are these: the proportion of combustible matter in the substance examined is previously found by calcination of another portion of the same; the actual quantity of oxygen employed in the deflagration is known by that of the oxymuriat used; the carbonic acid is absorbed by potash and its carbon estimated; the excess of oxygen is found by subsequent detonation with hydrogen; the hydrogen of the substance is presumed to form water with all the oxygen unaccounted for; and the azote exists in the residual azotic gas.

Fifteen vegetable substances were analyzed in this way, the particulars of some of which we shall give, and the results of the whole at the end of this article.

*Sugar.* 1000 parts of white sugar candy, exposed for many hours to a boiling water heat, lost only 8 parts of moisture. Some of the same sugar when calcined left only  $\frac{1}{11}$  of residue. The quantities used for the experiment were 300 parts of sugar (exclusive of the moisture and insoluble residue) and 7 times as much oxymuriat of potash, the oxygen of which was 627 parts (by weight). This oxygen was recovered, all but two parts, in 449.9 parts of carbonic acid containing 322 of oxygen, and in an excess of 303. of oxygen discovered by detonation with hydrogen. Therefore the 300 of sugar had in fact only consumed 322 of oxygen, all of which went to form carbonic acid, of which the carbon was 127.4; and as no other product from the sugar but carbonic acid and water appeared, it would follow that sugar is composed of 42.47 per cent. of carbon, and 57.53 of water, either as such, or of oxygen and hydrogen in the exact proportions required to form water.

*Gum Arabic, Starch, Sugar of Milk, Oak and Beech Wood*, all agree with sugar in being composed merely of carbon, and of oxygen and hydrogen in the proportions required to form water.

*Mucous Acid.* This acid was prepared by heating sugar of milk with nitric acid. The solution soon became turbid, and much mucous acid was deposited, which was well washed and dried in a boiling-water heat. This acid left no residue whatever after calcination. On deflagrating a given portion of it with four times its weight of oxygen in the above-mentioned apparatus, and estimating the oxygen and carbonic acid of the product, a considerable excess of oxygen above the quantity required to form water with the hydrogen of the mucous acid was found, and hence the acid is considered as composed of carbon, water, and oxygen in excess.

*Oxalic Acid.* This acid was not mixed immediately with the oxymuriat of potash, but was first combined with lime (by being saturated with ammonia and precipitated by muriat of lime) and the dried oxalat of lime was calcined by itself in a platina crucible, and thus found to consist of 61.345 of acid and 38.655 of lime.

A given portion of the oxalat of lime was then deflagrated in the usual way with  $1\frac{1}{2}$  its weight of the oxymuriat, and the results analyzed as before, but as a portion of the carbonic acid was retained in the deflagrating tube united with the lime and muriat of potash, this was separately analyzed by muriatic acid and the carbonic acid expelled.

*Tartareous Acid.* This acid was extracted in the usual way from tartrite of lime by sulphuric acid, but as it still retained a little of this latter acid even after repeated crystallization, it was dissolved in water and boiled with powdered litharge added gradually till the liquor no longer precipitated nitrat of barytes, by which means all the sulphuric acid was got rid of. The lead in solution was then separated by a current of sulphuretted hydrogen gas, and the clear liquid when evaporated gave pure tartareous acid. It was found impracticable however to make it into balls with oxymuriat of potash and water, as it deliquesced instantly on exposure to air.

The acid was therefore combined with lime, the tartrite of lime, dried at  $212^{\circ}$ , was found by calcination to consist of 77.577 of acid and 22.423 of lime, and this was further analyzed in the same manner as the oxalic acid.

*Citric Acid.* This was analyzed exactly as

the preceding acid. The citrat of lime consisted of 68.83 of acid and 31.17 of lime.

*Acetic Acid.* The acid here employed was first expelled from acetite of potash by sulphuric acid, and then heated with an excess of carbonat of barytes and the acetite of barytes evaporated and dried. But as this acetite could not be analyzed by simple calcination, (no continuance of heat being able to expell from the barytes all the carbonic acid formed by the combustion of the acetous) 30 grammes of the acetite were decomposed by sulphat of ammonia, and the sulphat of barytes was transferred, while still wet, to a platina crucible, and gradually ignited, till all the sulphat and acetite of ammonia adhering to it were expelled, and the sulphat of barytes remained pure. It weighed 25.443 grammes and contained 67 per cent. of barytes; and from these data acetite of barytes dried at  $212^{\circ}$ . consists of 43.17 acid and 56.83 barytes. This acetite was then deflagrated as the last, and the results examined.

All the acids here examined contained a notable excess of oxygen, as will be seen in the tabular statement at the end of this article.

*Resin of Turpentine, or Common Rosin.* This was simply mixed with 12 times its weight of the oxymuriat and deflagrated in the apparatus. Scarcely any carburetted hydrogen was produced by the combustion, but carbonic acid, and much water, which last when collected and examined was neither acid nor alkaline, and the residue in the tube was pure muriat of potash. The large quantity of water produced indicated a proportional excess of hydrogen in the resin, so that by the usual mode of estimation this resin contained carbon, oxygen and hydrogen in the proportions for constituting water, and an excess of hydrogen.

*Copal, Wax, and Olive Oil,* were analyzed in the same manner, some little difference being observed in the manipulation of mixing them with the oxymuriat.

From the analysis of the above fifteen vegetable substances the authors consider that the following important inferences may be deduced, namely:

That a vegetable substance is acid whenever the oxygen which it contains exists in a larger proportion than will constitute water with the hydrogen present.

That a vegetable substance is resinous, or oily, or alcoholic, &c. when the oxygen is in less proportion than is required to form water with the hydrogen.

That when the oxygen and hydrogen are in the exact proportions in which they constitute water, the vegetable substance is analogous to sugar, gum, fecula, ligneous fibre, &c.

The analysis of some of the primary *animal* substances was then undertaken. In this case there is another element, azote, which requires particular notice. Whenever any animal matter is deflagrated with an *excess* of oxymuriat of potash, a quantity of nitrous acid gas is formed, which is the greatest where the heat required for combustion is the lowest. This circumstance would render the analysis in the way above described much more complicated and uncertain, unless some method could be found of preventing the formation of nitric acid. This the authors assert is effectually done by lowering the dose of the oxymuriat, so that with this, neither ammonia, nor nitric acid is produced, but the whole products are azotic gas, water, carbonic acid, and oxycarburetted hydrogen, and with proper precautions even the latter compound may be almost entirely prevented, and nearly the whole of it changed to carbonic acid and water. The requisite proportions of oxymuriat of potash and the animal matter employed must be found by previous trials with successive quantities. The animal matter, long dried at 212°, must be mixed thoroughly, first with thrice its weight of the oxymuriat and thrown into a crucible barely red-hot. If the residue of the deflagration is black it will shew that there is too little oxymuriat, if it is white the quantity of this salt may be too much, if it is greyish the proportions are sufficiently correct; or at any rate neither nitric acid nor ammonia will be produced in the deflagration, though perhaps there will be some carburetted hydrogen. Whenever any gas contains along with this gas a certain proportion of azote and carbonic acid gas, the presence of these will prevent the entire combustion of the carburetted hydrogen with any oxygen that may be added. It will therefore be necessary to add a small quantity of pure hydrogen to produce the detonation of the carburetted hydrogen, and its total conversion into carbonic acid and water.

*Fibrine.* The fibrine collected from ox-blood by stirring it as soon as drawn, was dried by long exposure to boiling-water heat; and a portion of it calcined by itself left only  $\frac{1}{10}$  of fixed matter. Another portion was then mixed by long trituration with moist oxymuriat of potash, then made into balls and deflagrated in the same manner as the vegetable substances. The flame was very intense, and much water

condensed in the cooler part of the apparatus. The residue in the red hot tube was a white saline mass consisting only of muriat of potash with the incombustible part of the fibrine. The results after subsequent analysis gave for the constituents of fibrine, carbon, oxygen and hydrogen in the proportions of water, some excess of hydrogen, and azote. The exact quantities will be found in the table.

*Albumen* from white of egg, *Caseum* or the pure cheese of milk, and *Gelatine* were analyzed exactly in the same way, except that the oxymuriat was added to the gelatine in solution (its proportion of dry gelatine being known) and both were dried together by boiling-water heat, this being the only way in which the two could be intimately mixed.

The general result of the analysis of these four animal substances is; that they all contain even more carbon than sugar or gum does, that in all the hydrogen exceeds the proportion required to form water with the oxygen present, and that the azote also found is not far from the proportion required to form ammonia with the excess of hydrogen. Hence (supposing the small differences to arise from the unavoidable errors in the practical part of the experiments) it is not unlikely that these animal substances might be resolved into carbon, water and ammonia. In this point of view these animal matters will bear a strong analogy with sugar, mucilage, &c. inasmuch as each consists of carbon, and other constituent parts in the exact proportion in which they will unite into some definite compound, being carbon and water in the vegetable substances; and carbon, water, and ammonia in the animal.

The authors have not carried their experimental research further, but they suggest the probability of further analogies between the vegetable and animal principles in the animal acids and animal oils.

We shall not give the general observations which are suggested to the authors of these important experiments, but shall only add the tables of the actual results. It will be understood that the substances analyzed are taken, exclusive of their incombustible earthy metallic and saline contents, and that no azote is considered as entering into the vegetable principle. In the animal substances all the hydrogen and azote are estimated as constituting ammonia, allowing some excess or deficiency of this principle, to be attributable to accidental errors in the experiments.

Table of the constituent parts of the following Vegetable Substances.

Substance analyzed. 100 parts	Carbon.	Oxygen.	Hydrogen	Or supposing the Hydrogen and Oxygen to form water.		
				Carbon.	Water.	Oxygen in excess.
Sugar . . . . .	42.47	50.63	6.90	42.47	57.53	0
Gum Arabic . . . . .	42.23	50.84	6.93	42.23	57.77	0
Starch . . . . .	43.55	49.68	6.77	43.55	56.45	0
Sugar of Milk . . . . .	38.825	53.834	7.341	38.825	61.175	0
Oak wood . . . . .	52.53	41.78	5.69	52.53	47.47	0
Beech wood . . . . .	51.45	42.73	5.82	51.45	48.55	0
Mucous Acid . . . . .	33.69	62.67	3.62	33.69	30.16	36.15
Oxalic A. . . . .	26.57	70.69	2.74	26.57	22.87	50.56
Tartareous A. . . . .	21.05	69.32	6.63	21.05	56.24	20.71
Citric A. . . . .	33.81	59.86	6.33	33.81	52.75	13.44
Acetic A. . . . .	50.22	44.15	5.63	50.22	46.91	2.87
						Hydrogen in excess.
Rosin . . . . .	75.94	13.34	10.72	75.94	15.16	8.90
Copal . . . . .	76.81	10.61	12.58	76.81	12.05	11.14
Wax . . . . .	81.79	5.54	12.67	81.79	6.30	11.91
Olive Oil . . . . .	77.21	9.43	13.36	77.21	10.71	12.08

Table of the constituent parts of the following Animal Substances.

Substance analyzed. 100 parts	Carbon.	Oxygen.	Hydrogen	Azote.	Or, supposing the Oxygen to form Water with part of the Hydrogen, and the remain- der of the Hydrogen to form Ammonia with the Azote.			
					Carbon.	Water.	Ammonia	Azote, excess or deficiency.
Albumen	52.883	23.872	7.540	15.705	52.883	27.127	23.182	-3.191
Caseum	59.781	11.409	7.429	21.381	59.781	12.964	31.778	-4.623
Gelatine	47.881	27.207	7.914	16.998	47.881	30.917	22.743	-1.541
Fibrin	53.360	19.865	7.021	19.934	53.360	22.369	23.463	+0.808

**ANDALUSITE.** Feldspath Apyre H.

Its colour is flesh red verging on rose red. It occurs massive and crystallized in rectangular prisms. Its fracture is imperfectly foliated; the natural joints are parallel to the sides of a nearly rectangular prism, and to one of the diagonals of its transverse section. It is translucent; is harder than quartz, and sometimes even than spinelle. Sp. gr. 3.1.

It is infusible before the blow-pipe without addition. It is composed, according to Vauquelin, of

52. alumine  
38. silix  
8. potash  
2. oxide of iron

100.



This mineral in its crystalline form approaches very near to felspar, and in its analysis differs only in containing an excess of alumine; to this excess its hardness and infusibility are no doubt to be attributed. It was the opinion of Count Bournon (and M. Haüy seems inclined to agree with him) that andalusite is felspar intimately mixed with corundum.

It occurs in granite in Spain, France, Saxony, Ireland, and Devonshire.

#### ANTHOPHYLLITE.

This mineral has a perfectly foliated structure, and though not crystallized, is divisible in the direction of its natural joints, parallel to the sides of a rectangular prism; two of these sections present brightly shining surfaces, and are much more easily obtained than the others. Besides these four joints two others may be perceived on close inspection with a bright light, dividing the prism diagonally. Its specific gravity is 3.2. Its hardness is about equal to that of glass. Its colour is brownish, with more or less of a pseudo-metallic lustre. It affords by analysis, according to M. John,

62.66	silex
13.33	alumine
4.0	magnesia
12.0	oxide of iron
3.25	oxide of manganese
1.43	water
<hr/>	
96.67	

#### ANTIMONY.

##### § 1. Ores of.

##### Red Antimony.

This substance was supposed to be a native kermes or hydrosulphuret of antimony, but, according to a recent analysis by Klaproth,<sup>a</sup> it affords

67.5	antimony
10.8	oxygen
19.7	sulphur
<hr/>	
98.0	

##### Native Antimony.

A specimen of this substance from Andreasberg in the Hartz, has been analysed by Klaproth,<sup>b</sup> with the following result:

98.	antimony
1.	silver
0.25	iron
<hr/>	
99.25	

##### White Antimony.

A specimen of this mineral in quadrilateral tabular crystals, from Przibram in Bohemia, was analysed by Klaproth,<sup>c</sup> with the especial object of ascertaining whether it contained any muriatic acid as had been suspected by Haquet. For this purpose 25 grs. of the mineral were fused with 200 grs. of carbonated potash: the mass was then digested in water and the alkali was supersaturated by nitric acid. On the addition of nitrate of silver no precipitation took place, hence the white antimony may be considered as a pure oxide of antimony.

##### Antimony with Nickel.

This ore has hitherto been found only in a mine at Treusberg in Nassau.<sup>d</sup> It is composed in part of broad parallel plates of a shining white, resembling antimony, and in part of a compact leaden grey substance with a glimmering lustre. Its sp. gr. is 5.65. Its hardness is superior to that of grey antimony. When exposed on charcoal to the action of the blow-pipe it melts readily, and disengages white vapours of an arsenical odour, and which more or less adhere to the charcoal in form of a yellowish powder; by degrees the globule becomes less fusible, and there remains behind a white brittle refractory button.

By digestion in nitric acid a portion of the ore is converted into a yellowish white voluminous powder, and the remainder combines with the menstruum into a green liquor.

The powder, by digestion in muriatic acid slowly dissolves, with the exception of a small residue of a yellowish colour which consists of sulphur, of sand, and of a little arseniate of iron. This solution when diluted with water lets fall a white precipitate consisting of muriate of antimony and oxide of arsenic, inseparable from each other with perfect accuracy, according to Vauquelin, by any known chemical process, but in a considerable degree decomposable by distillation with sulphur which raises the principal part of the arsenic in the form of realgar. What remains in the retort is sulphuret of antimony with a little arsenic and lead.

The green nitric solution contains nickel, arsenic, and a little lead.

From the result of this examination, and from the different degree of fusibility exhibited by different portions of the ore, it is considered by Vauquelin as a mixture of sulphuret of antimony, of arsenical nickel, a little galena and iron pyrites.

<sup>a</sup> Klapr. Ess. ii. 147.

<sup>b</sup> Ann. de Chim. lxxxiii. p. 229.

<sup>c</sup> Ann. de Chim. lxxxv. p. 26.

<sup>d</sup> Haüy tab. comp. 299. Klapr. Ess. ii. 142.

The same ore has since been subjected to a careful analysis by Klaproth.\*

1. 300 grs. separated as accurately as possible from the oxide of iron with which it is naturally mixed, were digested in cold aqua regia, composed of 5 parts muriatic acid and 1 part nitric. The undissolved residue was again subjected to the same process, after which what remained undissolved was well washed in alcohol and dried. Its weight was 51 grs. of which 41 grs. burnt off with all the appearances attending the combustion of sulphur, leaving behind 10 grs. which dissolved entirely in aqua regia.

2. The solutions were mixed together in a retort and much concentrated; water being then added a copious precipitate fell down. The supernatant liquor was again concentrated, and a second precipitate was obtained as before by the addition of water.

3. After separating the precipitate the fluid was again concentrated, and appeared of a grass-green colour; ammonia was then added in excess which threw down a brown oxide of iron weighing after calcination 13.5 grs.

4. The ammoniacal solution was evaporated to dryness, and the saline mass gently ignited; the residue which had the appearance of yellowish brown micaceous scales was digested in muriatic acid, in which it entirely dissolved. By means of caustic potash a precipitate of an apple-green colour was obtained, which by calcination left behind 93.25 grs. of pure oxide of nickel of a slate grey colour, indicating 70.75 grs. of metallic nickel.

5. The precipitate N<sup>o</sup> 2, proved on examination to be arseniate of antimony, but all attempts at an accurate decomposition of it were fruitless.

Thus foiled, M. Klaproth had recourse to the following method. 200 grs. of the levigated ore were ignited with 600 grs. of nitre; the mass was then lixiviated and well washed. The lixivium on being slightly acidulated with nitric acid gave no precipitate, a proof that no antimony had been taken up. Lime water was then added and a voluminous precipitate of arseniate of lime fell down. This latter after being washed and dried was mixed with one-third of its weight of charcoal and sublimed in a retort, and afforded 22 grs. of metallic arsenic.

The matter insoluble in the lixivium was digested in aqua regia in which it dissolved almost entirely, and from this solution water

threw down a precipitate weighing 116 grs. equivalent to 89 grs. of metallic antimony.

Hence the constituent parts of this mineral, omitting the oxide of iron which is considered by M. Klaproth as accidental, are

25.25	metallic nickel
47.75	antimony
11.75	arsenic
15.25	sulphur
100.	

### § 2. Chemical Properties.

Much difference of opinion has arisen with regard to the number and composition of the oxyds of antimony. Thenard reckons as many as six, Proust only two. According to the latter chemist the lowest oxyd or *suboxyd* is composed of 81.5 metal to 18.5 oxygen or 22.7 oxygen upon 100 of metal; and the highest oxyd or *peroxyd* contains 77 metal to 23 oxygen; or 29.87 oxygen upon 100 of metal.

Pr. Berzelius reckons four oxyds of antimony, two of which have the characters of acids. We have not the particulars of the experiments, but the following are stated as the results:\*

The first or lowest oxyd is obtained by exposing antimony to the action of the positive side of the voltaic pile. It is grey, and when in contact with acids that do not themselves impart oxygen, part of the oxyd returns to the metallic state, and the rest passes to the second oxyd and dissolves.

The second oxyd is the base of emetic tartar, and most of the other antimonial salts. This is white and fusible.

The third oxyd is also white but infusible at a white heat. It possesses all the characters of an acid, and is called by the author *Stibious Acid*. The white oxyd of antimony by nitre is in fact a salt composed of potash with an excess of this stibious acid, and is decomposed by boiling water into a neutral soluble stibiate of potash, and an insoluble portion with still greater excess of acid. From this soluble stibiate of potash professor Berzelius has formed many other neutral stibiates.

The fourth oxyd is straw coloured and is an acid with higher oxydation than the former, and therefore has the name of *Stibic Acid*. At a high temperature it gives out oxygen and passes to the state of *Stibious Acid*.

\* Klapr. Ess. ii. 134.

\* An. Chim. tom. 83, p. 169.

The respective proportions of metal and oxygen in these compounds are the following.

The second oxyd contains 100. antimony to 18.6 oxygen.

The third oxyd contains 100. antimony to 27.9 oxygen.

The fourth oxyd contains 100. antimony to 37.2 oxygen.

These three oxyds therefore have their oxygen in the proportions of 1,  $1\frac{1}{2}$  and 2.

The elements of the first oxyd are not given. It may be presumed (according to the theory of definite proportions) to contain either 9.3 or  $\frac{9.3}{2} = 4.65$  oxygen to 100. of metal.

The same author also gives for the elements of the sulphuret of antimony, 100. of antimony to 37.25 of sulphur.

*Tartarized Antimony.—Tartar Emetic.*

A very elaborate examination of this salt and of the various modes of preparing it, has been given by a practical chemist, Mr. R. Phillips,<sup>b</sup> who has shewn the great uncertainty of success in following the mode laid down by the London College of Physicians in their last Pharmacopœia. This uncertainty arises from the strong tendency in this metal to pass from the state of suboxyd (in which alone it is soluble in tartar) to that of insoluble peroxyd. Mr. Phillips has given as an improvement in the process, the employment of the sub-sulphat of antimony as the base to be afterwards boiled with a solution of an equal weight of cream of tartar, which crystallizes with the tartar into the tartarized antimony, or triple tartrate of antimony and potash. The sub-sulphat is prepared by boiling and evaporating to dryness a mixture of sulphuric acid with about half its weight of metallic antimony, and afterwards washing out of the residue all the uncombined sulphuric acid, leaving a tasteless sub-sulphat, in which the oxyd must be at a low state of oxydation, since it dissolves copiously with tartar and forms with it the tartar emetic. As all tartar contains tartrate of lime, some sulphat of lime is also produced by the acid of the sub-sulphat, which partly crystallizes along with the emetic tartar, but is separated by a second solution.

APLOME.

This mineral occurs in rhomboidal dodecahedrons of a deep brown colour inclining more or less to orange, striated externally parallel to the short diagonals of the rhombs. On ex-

posing fragments of this substance to a bright light, indications of laminae may be perceived, the direction of which, combined with that of the striæ, affords reason for supposing that its primitive form is a cube. Its specific gravity is 3.44. It scratches quartz though slightly. Its fracture is uneven, passing into small conchoidal with a moderate lustre. It is opaque and in very minute crystals translucent. Before the blow-pipe it is fusible into a blackish glass. It affords by analysis, according to Laugier,

40.	silex
20.	alumine
14.5	oxyd of iron
14.5	lime
2.	oxyd of manganese
2.	ferruginous silex
2.	volatile matter

95.0

It occurs in Siberia on the banks of the river Lena.

APOPHYLLITE. See ICHTHYOPHTHALMITE.

ARCTIZITE. See WERNERITE.

ARENDAHITE. See STRAHLSTEIN, glassy.

ARGIL, native.

A small portion of this mineral, not sufficient for a regular analysis, was examined by Fourcroy, who states it to contain about 24 per cent. of sulphate of lime (Ann. de Mus. I. 45); since which it has been formally analyzed by M. Simon of Berlin, and by Bucholz, with the following results.<sup>a</sup>

Simon.	Bucholz.
32.5 —	31.0 alumine
19.25 —	21.5 sulphuric acid
0.45 —	2.0 oxyd of iron
0.35 —	
0.45 —	silex
47. —	45. water

100.00 — 99.5

ARSENIC.—ARSENICATED HYDROGEN. ARSENIATS.

§ 1. Ores of Arsenic.

*Mispickel.*

Some recent experiments on this ore have been made by M. Chevreul.<sup>b</sup> When mispickel is heated in a glass retort, there rises a sublimate consisting of metallic arsenic with a very small portion of orpiment, and the residue

<sup>a</sup> Experimental Examination of the Pharmacopœia. a Klapp. Dict. Chim. art. *Alumine natives.*

<sup>b</sup> Journ. des Mines, xxix. p. 459.

consists of sulphuret of iron, retaining some traces of arsenic. The component parts of this ore, as deduced from a separate analysis of the sublimate and of the residue, are

43.418 arsenic
34.938 iron
20.134 sulphur
<hr style="width: 100%;"/>
98.490

Iron is well known to have a stronger affinity for sulphur than arsenic has, and as in the present instance the proportion of iron and sulphur is just sufficient to form the sub-sulphuret, it appears probable that mispickel is a combination of iron pyrites and of metallic arsenic.

*Arsenical Pyrites.*<sup>c</sup>

The primitive form of this substance is a strait rhomboidal prism, the angles of which are alternately 111°-18' and 68°-42'.

It is composed, according to Lampadius, of

58.9 iron
42.1 arsenic
<hr style="width: 100%;"/>
101.0

§ 2. *Chemical Properties.*

It is often desirable to detect minute quantities of arsenic mixed with other substances. Some of these means have been already mentioned under this article, (*Ch. Dict. I. p. 105.*) but another should be noticed on account of the great extent of its operation. It consists in first dissolving the arsenic in water, adding a small quantity of sub-carbonat of potash, and then applying nitrat of silver. The process is thus described by Mr. Hume who first suggested it.<sup>d</sup> Put in a glass flask two or three grains of the powder suspected to be arsenic, add eight ounces of distilled water and gradually bring it to boil over a lamp or clear fire. Then add a grain or two of sub-carbonat of potash or soda, and shake the mixture. When clear, pour some of the solution into a glass, and dip just under the surface of the liquid a stick of lunar caustic, and a beautiful yellow precipitate will appear, which can hardly be confounded with any other substance.

Dr. Marcet<sup>e</sup> has given a variation of this process which has the advantage of being performed in a few seconds. Pour some of the

clear fluid suspected to contain arsenic into any glass vessel, stir into it a glass rod dipped in pure ammonia, and immediately after another glass rod wetted with nitrat of silver. The same orange yellow precipitate will immediately appear. Care should be taken to add only a very small quantity of each of the reagents, particularly of the ammonia. In either mode it is obvious that any muriatic acid present will give a precipitate with nitrat of silver, and this metallic salt will also be decomposed by the carbonated potash or soda where this method is used, so that it is not the mere appearance of any precipitate, but of an *orange-yellow* precipitate that will determine the presence of arsenic. Where the arsenic is in the state of arsenic acid the colour of the precipitate will be brick-red.

This precipitate is a compound of oxyd of silver and arsenic, either partially or entirely oxydated, and when heated *per se*, especially on charcoal, the arsenic sublimes and leaves a globule of pure silver.

*Orpiment and Realgar.* The following distinctive characters of these substances are given by M. Thenard.<sup>f</sup>

Both of them melt and sublime unaltered in close vessels and without giving out any sulphureous acid. Both are acted on by the sulphuric nitric and oxymuriatic acids. Sulphuric acid acts much more easily on orpiment than on realgar. In both cases sulphureous acid and arsenious acid are formed, but more of the former acid and less of the latter are produced with orpiment than with realgar. Nitric acid is easily decomposed even without heat on both these substances, and sulphur and arsenious acid are formed. The fixed alkalies dissolve both without heat; when potash is used, hydro-sulphuret of potash and arsenite of potash are formed, for on adding lime-water to the solution a copious white precipitate appears, which, when treated with carbonat of potash, gives a liquid that yields abundance of arsenious acid on saturation with muriatic acid and evaporation.

Sulphur fused with realgar converts it into orpiment, and arsenic added to orpiment changes it to realgar. Three parts of sulphur and four of arsenic form orpiment: and one part of sulphur with three of arsenic form realgar. The latter is the most fusible of the two. Orpiment made artificially by sublimation is

<sup>a</sup> Haüy. Table Comp. 95, 272. <sup>d</sup> Phil. Mag. vol. 33. <sup>e</sup> Medico-Chirurgical Transact. vol. 2, p. 15, and vol. 3. 313. <sup>f</sup> An. Chim. No. 177. p. 284.

yellow and transparent as is native orpiment after being melted; but both assume a very bright clear yellow when reduced to powder. The orpiment produced in the moist way by a soluble arsenite, a hydro-sulphuret, and an acid, is always of the same opaque bright yellow as the other orpiment when pulverized.

*Arsenic Acid. Arsenious Acid. Arsenite, and Arseniate of Lead.*

According to the experiments of Proust, 100 parts of arsenic combine with 33 of oxygen to form the white oxyd, or the *Arsenious Acid*, and with 53 of oxygen to form the *Arsenic acid*. This subject has been examined by professor Berzelius with the view of accommodating these numbers to the system of definite proportions explained under the article AFFINITY in this appendix. It is there assumed that when any base is capable of more than one degree of oxygenation, the lowest number multiplied by 2, 3, &c. or by the intermediate halves  $1\frac{1}{2}$ ,  $2\frac{1}{2}$ , &c. will give all the other degrees. Hence the oxygen of arsenious acid must bear one or other of these proportions to that of arsenic acid. Another rule is, that when a compound consists of two oxydated substances the oxygen of the base must bear an equally definite proportion with that of the acid; hence in any of the metallic arseniates (arseniat of lead for example) the oxygen of the arsenic acid must bear a definite and simple proportion to that of the oxyd of lead. Both these questions are here examined.\*

Arsenious acid contains, according to Proust, 33.33 of oxygen to 100. metal, and arsenic acid contains 53 oxygen to 100. metal, and other chemists give rather less. The nearest definite proportion between these is  $1\frac{1}{2}$  times 33, which gives 50. The following are professor Berzelius's experiments.

200 parts of sub-oxyd of lead dissolved in nitric acid, evaporated to expell the excess of acid and again dissolved in water, were precipitated by *arsenite* of potash. The precipitate of arsenite of lead, which was at first light and flocculent, easily separated by boiling, and when dried weighed 391.26, but on being ignited gave out 6.65 of water and 16.51 of uncombined arsenious acid. The neutral salt remaining weighed 368.1.

A similar experiment gave arsenite of lead in the proportion of 368.8. Hence the composition of arsenite of lead, taking the former estimate, is

Arsenious acid .	45.667	—	100.000
Sub-oxyd of lead .	54.333	—	118.977
			<hr/>
			100.000 — 218.977

Sub-oxyd of lead was found from very careful experiments to contain 7.15 per cent. of oxygen, and therefore the 118.977 contain 8.5068 oxygen. Hence the 100. of arsenious acid must contain some proportion of oxygen, which is a simple multiple of 8.5068, and as three times this quantity very nearly agrees with the experiments of Proust, arsenious acid is assumed to be composed of,

Arsenic . .	74.48	—	100.000
Oxygen . .	25.52	—	34.263
			<hr/>
			100.00 — 134.263

The composition of the arsenic acid is also deduced from its combination with lead.

100. parts of arseniat of lead were dissolved in nitric acid, and precipitated by sulphat of ammonia. The supernatant liquor was evaporated to dryness to expell the excess of nitric acid, and the soluble portion was again dissolved in water and completely neutralized by ammonia. This separated a little sulphat of lead which was added to the other portion that remained insoluble in water. The whole sulphat of lead thus obtained was 95.59. A second experiment gave nearly similar results. This quantity of sulphat of lead much exceeded that obtained by Klaproth and Rose, by the simple addition of sulphat of ammonia to arseniat of lead in nitric acid, but professor Berzelius shews that these eminent chemists were not aware of the solubility of a portion of the sulphat of lead in the excess of acid.

Hence arseniate of lead consists of,

Arsenic acid .	29.6317	—	100.0
Sub-oxyd of lead	70.3683	—	237.5
			<hr/>
			100.0000 — 337.5

The 237.5 of sub-oxyd of lead contain 16.981 of oxygen. Hence the composition of 100. parts of arsenic acid (according to the rules before laid down) must contain such a portion of oxygen as is produced by a simple multiplication of 16.981, and at the same time will afford such a proportion between the metal and the oxygen as will give an increase of oxygen upon 100. parts of the metal, in a simple (or nearly simple) ratio to the oxygen.

\* An. Chim. tom. 80. p. 9.

of the arsenious acid which is 34.263. These conditions will be fulfilled (making a reasonable allowance for errors) by taking the oxygen in 100. parts of arsenic acid as double that of the sub-oxyd of lead with which it is saturated, that is,  $16.981 \times 2 = 33.962$ .

Arsenic acid will therefore contain,	
Arsenic . .	66.038 — 100
Oxygen . .	33.962 — 51.428
	100.000 — 151.428

And as the arsenious acid contains 34.263 oxygen to 100. of metal, the arsenic acid will contain to the same quantity of metal  $1\frac{1}{2}$  times  $34.263 = 51.3945$ , within a very small difference.

It has been already mentioned, under the article *affinity*, that wherever the ratio between two portions of the same substance that unite to another substance is expressed by a fraction (as  $1\frac{1}{2}$ ) there is reason to suppose some *minimum* of combination which will convert these fractional numbers to integers. This in the present instance will be produced by assuming the *minimum* of oxydation of arsenic, as either half or a quarter of that of the arsenious acid. It is well known that when metallic arsenic is exposed to the air it loses its lustre and becomes covered with a blackish brown powder. The author exposed 200. parts of metallic arsenic for two months to the air, at the end of which time it entirely fell into a bulky black powder. The increase of weight in that time was 16.2, and in another month the further increase was only 0.75, being in all 16.95, or in the proportion of 8.475 oxygen to 100. of metal, and  $8.475 \times 6 = 50.85$ , which does not much differ from 51.428, the highest term of oxygenation. Hence it is probable that the arsenious acid is 4 times the *minimum* of oxygenation, and the arsenic acid 6 times.

The *Arsenite of Lead* mentioned above has the following properties: when dry it is white, and by friction it becomes apparently even more electric than sulphur. When melted it is transparent, and remains so after cooling and then becomes yellowish, but of a dark green if any copper is present. Arsenite of lead kept at a red heat gives out arsenious acid, and is gradually changed to arseniate of lead.

#### *Arsenicated Hydrogen.*

Under the article *Alkaline Basis* in this appendix we have mentioned the alloy of potassium and arsenic, and the production of

arsenicated hydrogen by adding water to this alloy. It was there found that when 100 parts of arsenicated hydrogen are kept in contact with melted tin, the latter extracts all the arsenic and then the hydrogen expands to 140 parts. (*See the above article.*)

#### ASPARAGUS.

The juice of this plant has been examined with much care and skill by M. Robriquet.\* A quantity of asparagus was first bruised and the juice extracted by pressure, and passed through a coarse cloth, leaving a fecula behind. The juice in this state had a strong unpleasant smell, and was a dirty yellow colour inclining to green. The fecula, treated by boiling alcohol, only partially dissolved, and the insoluble portion examined in various ways strongly resembled animal gluten, in drying to a horny mass which by combustion gave much ammonia. The part soluble in hot alcohol deposited on cooling a substance a good deal like wax; whilst the supernatant solution contained a species of resin.

The filtered recent asparagus juice was sensibly acid and reddened litmus. After boiling, to separate some remaining flocculi of albumen, it was evaporated nearly to dryness, and then digested with alcohol, and the part untouched by this agent was dissolved in water. The alcoholic solution gave a very slight precipitate with acetite of lead, and this metallic precipitate was not again soluble in distilled vinegar, thus shewing that the acid of the asparagus-juice was not the malic. Another portion of the juice was assayed by distillation with sulphuric acid, and a quantity of acetic acid united with potash was obtained. Still the acid of the juice was not clearly made out, and it was afterwards analyzed with great attention. To obtain it pure the expressed juice of the plant was first coagulated by heat, and the clear liquor filtered. Into this liquor was poured acetite of lead as long as any precipitate formed, and this last when well washed was digested with a third of its weight of sulphuric acid diluted with three parts of water, and moderately heated. The sulphat of lead thus formed remained at the bottom, and the clear supernatant liquor was evaporated to an extractive consistence, and treated with alcohol twice successively (excluding a little insoluble matter each time) till a clear solution in the spirit was obtained. This acid was brownish, had a very sour taste mixed with some unpleasant flavour particularly when heated, and gave soluble salts with the alkalis and insoluble

\* An. Chim. tom. 55.

ones with the earths. It decomposed the earthy acetites by simple affinity, and also many metallic salts, particularly those of iron, copper and lead, and the salt produced by its mixture with acetite of lead was in the form of white flocculi *insoluble* in distilled vinegar. In this last property it differed decisively from the malic acid, and also in decomposing the sulphats and acetites of iron and copper. To ascertain the nature of this acid of asparagus-juice it was precipitated by lime-water, and the washed precipitate calcined in a silver crucible till all the carbonaceous matter had disappeared, and a grey calcareous salt remained insoluble in water. This was boiled and dissolved in distilled vinegar and precipitated unaltered by ammonia, and then was found to be *phosphat of lime*.

To prove still further that this supposed peculiar acid is the phosphoric, its combination with lead (made by precipitating acetite of lead) was fused with the blow-pipe, and the button assumed on cooling that polyhedral form which is so characteristic of *phosphat of lead*.

Asparagus-juice does however contain some peculiar substances. A quantity of the juice was concentrated and left for a considerable time to itself in M. Vauquelin's laboratory. After a while a good many crystals formed in the liquor, obviously of two distinct kinds, which were examined by Messrs. Vauquelin and Robriquet.<sup>b</sup>

One of these (which indeed had before been noticed by M. Robriquet) had the following properties:

When obtained pure by repeated crystallization it assumes the form of rhomboidal prisms. It is quite white, moderately soluble in water, and neither acid nor alkaline; infusion of galls, acetite of lead, oxalat of ammonia, muriat of barytes, and hydro-sulphuret of barytes, produce no change in it: it is insoluble in alcohol. It contains neither ammonia nor earth: when ignited *per se* in a platina crucible, it swells up and exhales pungent vapours, and leaves a bulky coal but absolutely insipid, and the ash is not in the least degree alkaline. Nitric acid decomposes this salt and produces a yellow bitter liquor containing much ammonia formed in the process.

This salt therefore seems at present to be a peculiar crystallizable substance containing none of the known acids, alkalies, earths, or other salifiable bases.

The other crystals formed in the asparagus liquor were equally white, but soft and imperfectly crystallized in fine needles having a sensibly saccharine taste, like that of manna. It has not been further examined.

## AUGITE.

In addition to the analysis of the Volcanic Augite from Etna by Vauquelin, already cited, we now have analyses of the Augite of Frascati,<sup>c</sup> and of Giuliana<sup>d</sup> in Sicily by Klaproth.

Fras.	Giul.	
48.	—	55. silex
24.	—	10. lime
8.75	—	1.75 magnesia
5.	—	16.5 alumine
12.	—	13.75 oxyd of iron
1.	—	— oxyd of manganase
a trace	—	— potash
—	—	1.5 water
<hr/>	<hr/>	
98.75	—	98.5
<hr/>	<hr/>	

The Norwegian Augite has also been analyzed by Simon and Roux<sup>e</sup> with the following results.

Simon	Roux	
50.25	—	45. silex
25.5	—	30.5 lime
3.5	—	3. alumine
7.	—	— magnesia
10.5	—	16. oxyd of iron
2.25	—	5. oxyd of manganase
0.5	—	— water
a trace	—	— chrome
<hr/>	<hr/>	
99.5	—	99.5
<hr/>	<hr/>	

On examining however the details of the analysis by M. Roux, it is manifest that he failed to precipitate the whole of the alumine, and that the whole of the magnesia was left in the lime.

Var. 1. Coccolite, *Korniger Augit*, *Kars-ten*.

Its colour is a deep green; it presents an assemblage of slightly coherent granular concretions of various sizes up to that of a small pea, several of which resemble crystals with their solid angles worn off, and M. Haüy, by mechanical division, has actually reduced them to tetrahedral prisms. Internally this mineral is shining with a vitreous lustre; its fracture is foliated; it is translucent, scratches glass, and gives a few sparks with steel. Sp. gr. 3.3.

It is infusible by the blowpipe without ad-

<sup>b</sup> An. Chim. tom. 55.<sup>c</sup> An. Chim. lxxvii. 225.<sup>d</sup> Klapr. Dict. de Chim.<sup>e</sup> Journ. de Mines.

dition; with soda it forms an olive green slaggy glass, and with borax a pale yellow semitransparent glass. It has been analyzed by Vauquelin, and appears to consist of

50.	silex
24.	lime
10.	magnesia
1.5	alumine
7.	oxyd of iron
3.	oxyd of manganese
<hr/>	
95.5	
4.5	loss

It occurs in the iron mines of Sudermania; and of Arendahl in Norway.

Var. 2. *Sahlite*. Malacolite, *D'Andrada*.

Its colour is pale greyish green; its external lustre is vitreous approaching to waxy; it is translucent; it scratches glass slightly, but gives no sparks with steel, and is easily frangible. Fracture shining and strait lamellar with a triple cleavage. It is generally in the form of coarsely granular distinct concretions, but also occurs massive with a broad lamellar fracture, or crystallized in rectangular parallelepipeds slightly bevelled on their lateral edges, or in prisms terminated by convex planes. Sp. gr. 3.23.

It is infusible before the blowpipe without addition.

It occurs in Sweden at the silver mines of Sahla; and at Buoen in Norway.

Its component parts, according to an analysis by Vauquelin, are

53.	silex
20.	lime
19.	magnesia
3.	alumine
4.	oxyds of iron and of manganese
<hr/>	
99.	
1.	loss.

To this variety, on the authority of M. Haüy, are also to be referred the Mussite and Alalite of M. Bonvoisin, of which M. Haüy had once formed a new species under the name Diopside.\*

Its colour is greenish or yellowish white: it occurs crystallized in tetrahedral and dodecahedral prisms, or in deeply striated sub-cylindrical grains, or massive with a lamellar fracture. It scarcely scratches glass, and is fusible before the blowpipe into a greyish mass. It is composed, according to Laugier, of

\* Journ. des Mines, No. 115.

57.	silex
16.5	lime
18.25	magnesia
6.	oxyds of iron and of manganese
<hr/>	
97.75	
2.25	loss.

The Mussite occurs in the Commune of Balme-de-Mussa, Department of the Po, in a vein accompanied by granular carbonate of lime.

The Alalite occurs near the village of Ala, in the mountain of Ciarmetta, in a vein accompanied by garnets.

AUTOMOLITE. *Spinelle zincifère*, II.

This substance occurs only crystallized. Its primitive form is the regular octohedron, besides which it presents the transposed octohedron. The crystals are for the most part very small, rarely equalling in size a small nut. Its specific gravity is 4.69 (4.26 Ekeberg). It scratches quartz. Its colour is a deep bluish-green: the entire crystals are opaque, but in thin fragments it is more or less semi-transparent. Its fracture is lamellar, parallel to the faces of the crystal, but in other directions is uneven and scaly with a vitreous lustre.

Before the blowpipe it neither melts nor undergoes any change of colour. With phosphate of soda it runs into a clear colourless bead.

It was first analyzed by Ekeberg, and afterwards by Vauquelin, with the following results.

Ekeb.	Vauq.
60.	— 42. alumine
4.	— 4. silex
24.	— 28. oxyd of zinc
9.	— 5. oxyd of iron
0.	— 17. sulphur
0.	— 4. portion of the mineral remaining unaltered
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97.	100.

It occurs at Falun in Sweden.

It was at first supposed to be corundum mixed with zinc, but the prevailing opinion at present is that it is spinelle pleonaste loaded with blende.

AZOTE WITH OXYGEN, *Compounds of*. The specific gravity of azotic gas is to that of hydrogen, as 13 to 1.<sup>b</sup> 100 cubic inches of it at a mean temperature and pressure, weigh between 29. and 30. grains.

There are at least three specific compounds of azote and oxygen; viz. Nitrous Oxyd, Nitrous Gas, and Nitrous Acid Gas.

<sup>b</sup> Davy's Elements.



*Nitrous Oxyd.* The specific gravity of this gas is to that of hydrogen as 21. to 1; and 100. cubic inches weigh between 48 and 49 grains. When one cubic inch of nitrous oxyd is mixed with the same quantity of hydrogen and exploded by the electric spark, water is formed, and the only residue is one cubic inch of azote. Now as one cubic inch of hydrogen requires half a cubic inch of oxygen to become water, it follows that one cubic inch of nitrous oxyd contains one cubic inch of azote and half a cubic inch of oxygen, condensed into the space of a single cubic inch.

In like manner, if dry charcoal be ignited in one cubic inch of nitrous oxyd, the products are half a cubic inch of carbonic acid and one cubic inch of azote. Hence, as oxygen neither gains nor loses in bulk by its conversion into carbonic acid, the composition of nitrous oxyd is found, as before, to be two volumes of azote and one of oxygen, condensed into the space of two volumes. Hence too it consists, by weight, of 26 of azote and 15 of oxygen.

*Nitrous Gas.* Its specific gravity is to that of hydrogen as 14 to 1; and 100 cubic inches weigh about 32 grains. When several metals, such as arsenic, zinc, or potassium, are heated in nitrous gas, it oxydates them and affords half its volume of azote. If charcoal is ignited in two cubic inches of nitrous gas, the products are one cubic inch of carbonic acid and one of azote. Hence as oxygen gas neither expands nor contracts by conversion into carbonic acid gas, nitrous gas consists of equal volumes of azote and oxygen not condensed by their chemical union; or it contains (by weight) 13 parts of azote to 15 of oxygen. When two cubic inches of nitrous gas are exposed to the action of muriat of tin, or sulphuretted alkali, part of the oxygen of the gas is absorbed, and one cubic inch of nitrous oxyd is left, which exactly harmonizes with their relative proportions of oxygen and azote; for one cubic inch of nitrous oxyd contains, as already mentioned, one cubic inch of azote and half a cubic inch of oxygen; and therefore the portion of oxygen extracted by the sulphuret is exactly half a cubic inch of oxygen.

*Nitrous Acid Gas.* When oxygen and nitrous gas are mixed together, red fumes of *nitrous acid gas* are produced, and a condensation of the bulk of the gasses takes place. If the experiment be made over water, a rapid and total absorption takes place, and the water becomes acidulous. Much difference of opinion

still exists as to the respective proportions in which nitrous gas and oxygen unite, nor is it very easy to make accurate experiments, since the acid gas is absorbed both by water and mercury.

According to Sir H. Davy, when two volumes of nitrous gas and one volume of oxygen, both previously dried, are mixed together in a vessel exhausted of air, they become condensed to half their volume, and form a deep orange-coloured gas, which is nitrous acid gas. Calculating from the condensation, the specific gravity of this gas must be to that of hydrogen as about 28. to 1; and 100 grains of it must weigh 65.3 grains. When water is admitted to this gas there is a rapid absorption, and the water gains a tint of green. This proportion of two volumes of nitrous gas to one volume of oxygen is the highest in oxygenation that can be produced as a pure and distinct gaseous body; for when the oxygen is actually mixed in greater proportion, the condensation is such as only to indicate the formation of the above nitrous acid gas, with an excess of uncombined oxygen. The same happens when water is admitted, the acid gas absorbed retaining no greater a proportion of oxygen than when in a gaseous state. But on the other hand, when this nitrous acid gas is absorbed by an alkaline base, a portion of nitrous gas is always evolved, leaving the remainder in a state of a higher relative oxygenation than gaseous nitric acid. This the author concludes from many experiments to be in the proportion of 2 volumes of nitrous gas and  $1\frac{1}{2}$  of oxygen, and this forms the *pale nitric acid* as it exists in solution in water, or as the acid part of the alkaline, earthy, and metallic nitrats. Nitric acid therefore, according to this opinion, when once obtained from the decomposition of the nitrats can exist unchanged in solution in water; though water alone cannot condense from its gaseous state a mixture of two volumes of nitrous gas and  $1\frac{1}{2}$  of oxygen, which is here given as the composition of nitric acid. This liquid acid again may be made to absorb different quantities of nitrous gas, when it becomes yellow, orange, blue, and finally blueish-green, when saturated with nitrous gas.

It has been mentioned that oxygen and nitrous gas unite in different proportions, and these are in a good measure regulated by the quantities of each gas employed, and the diameter of the vessel in which they are mixed. Mr. Dalton gives the following interesting re-

sults of his own experience on this subject.\* When two measures of nitrous gas are put to one measure of oxygen gas in a tube one-third of an inch in diameter and five inches in length, standing over water, as soon as the diminution has apparently ceased, which will be in half a minute, if the residuary gas is transferred into another tube, it will be found that one measure of oxygen and 1.8 of nitrous gas have disappeared.

When 4 measures of oxygen are put to 1.3 of nitrous gas in a tube two-tenths of an inch in diameter and ten inches long so as to fill it, it will be found that 1 measure of oxygen will combine with 1.3 of nitrous gas in four or five minutes.

When 1 measure of oxygen and 5 of nitrous gas are mixed together so as to form a thin stratum of air not more than  $\frac{1}{8}$ th of an inch in depth (as under a common tumbler) the oxygen will take up from 3 to  $3\frac{1}{2}$  measures of nitrous gas in a moment, without any agitation. If

measure	measures	
1	.9	nitrous gas form oxynitric acid
1	1.8	nitric acid
1	3.6	nitrous acid

And all the intermediate degrees of saturation are considered as mixtures of two or more of the above compounds.

One of the most important considerations relative to nitric acid is the determination of the quantity of real acid in a watery solution of a given specific gravity. The temperature of ebullition of nitric acid of different densities varies in a very singular manner. When weak nitric acid is boiled or distilled, the weakest portion comes over first; but when the acid is concentrated, the strongest portion comes over first, as observed by Dr. R. Perceval (*see Chim. Dict. art. Nitric acid*). From these facts, Mr. Dalton inferred that an acid of some one strength, and only one, was incapable of any change of strength by distillation, so that when a portion of this was distilled, the distilled part and the residue would have the same specific gravity. It was desirable to find the actual strength of this acid, as these circumstances shew a nice adjustment of affinities between the acid and the water; and this acid Mr. Dalton has found by many experiments to be of the specific gravity of 1.42. The boiling temperature of this acid is higher than that of any other nitric acid, stronger or weaker, being  $248^{\circ}$ , which indeed is the immediate reason of the

equal measures are mixed, then 1 oxygen takes about 2.2 nitrous gas.

Thus it appears that these two gasses will unite in a great variety of proportions, according to the relative quantity of either gas employed, and the suddenness of their union. But according to Mr. Dalton, there is however a definite *maximum* and *minimum* of saturation, which includes all the other proportions. The *maximum* of oxygenation actually observed is that in which 1 measure of oxygen combines with 1.3 of nitrous gas; and the *minimum* is that of 1 measure of oxygen to 3.6 of nitrous gas; but as the actual maximum does not harmonize with any definite proportion, Mr. D. assumes hypothetically the real *maximum* to be 1 of oxygen with .9 of nitrous gas, to which he gives the term *oxynitric acid*. The constitution of nitric acid he infers from other observations to be 1 measure of oxygen to 1.8 of nitrous gas. Hence all the compounds of nitrous gas and oxygen will be thus expressed:

reduction of strength of all the other nitric acids to that of 1.42 when submitted to gradual distillation; and of the stronger acids parting with the portion above 1.42 and the weaker acids with that below this standard. Hence the continued boiling of any nitric acid tends to bring the portion in the retort to the specific gravity of 1.42, and to raise the temperature to  $248^{\circ}$ . Mr. Dalton calculates this acid of 1.42 to be composed of 2 atoms of water to 1 atom of real acid. The acid of 1 of real acid to 4 of water has the specific gravity of 1.30, and is remarkable for freezing the most easily of all, namely at  $-2^{\circ}$ , according to Mr. Cavendish.

With respect to the quantity of real acid in a solution of given specific gravity, Mr. Dalton follows the method employed by Kirwan, assuming that fused nitre consists of 47.5 per cent. by weight of real acid and 52.5 of potash. Mr. Dalton's estimate of the real acid of different mixtures of nitric acid and water, agrees very nearly with those of Mr. Kirwan, but Mr. D. has given the important addition of the boiling temperature of each. The following is his table of the quantity of real acid in 100 parts of liquid nitric acid at the temperature of  $60^{\circ}$ .

\* New System, part ii. p. 327.

Acid per cent. by weight.	Acid per cent. by measure.	Specific gravity.	Boiling point.
100	175?	1.75?	30°?
82.7	134	1.62	100°
72.5	112	1.54	175°
68	102	1.50	210°
58.4	84.7	1.45	240°
54.4	77.2	1.42	248°
51.2	71.7	1.40	247°
44.3	59.8	1.35	242°
37.4	48.6	1.30	236°
32.3	40.7	1.26	232°
28.5	34.8	1.22	229°
25.4	30.5	1.20	226°
23	27.1	1.18	223°
21	24.6	1.17	221°
19.3	22.4	1.16	220°
17.8	20.5	1.15	219°
16.6	18.9	1.14	219°

M. Gay Lussac,<sup>d</sup> in repeating Mr. Dalton's experiments on the different proportions of oxygen absorbed by nitrous gas according to the circumstances of the experiment, has endeavoured to reduce all the definite combinations of azote and oxygen to very simple numbers, estimating the gasses by measure.

Nitrous gas is composed of equal volumes of azote and oxygen, which unite without condensation; and the author considers nitric acid as composed of 200 measures of nitrous gas and 100 measures of oxygen, or (what amounts to the same) it consists of 100 measures of azote to 200 of oxygen. The intermediate term of saturation is that which constitutes *nitrous acid gas*, and which when absorbed by water gives the *liquid nitrous acid*, the acid part of the *nitrites*. The author finds, agreeably to Mr. Dalton's experiments, that the production of this intermediate acid depends on the circumstances of the experiment and the proportions of each gas employed. If 200 measures of nitrous gas are put into a narrow tube over water, and 200 measures of oxygen are added, or if this order is reversed, and the oxygen added first, 500 measures will disappear and 100. measures of oxygen will remain unaltered. The water that has absorbed these 300 measures will be a solution of *nitric acid*, and with potash will form common nitre. Therefore nitric acid contains 2 parts by measure of nitrous gas to one of oxygen. But if the oxygen be not in excess, if for example 100 measures of oxygen be added to 400. measures of nitrous

gas, the entire absorption will be 400 measures, and 100 measures of nitrous gas will remain. The water that has absorbed these 400 measures will now be *nitrous acid*, and with potash will form small needled crystals of *nitrite of potash*, which give out copious red fumes on the addition of any strong acid. To make this experiment correctly it should be in a wide vessel and without agitation, so that the water in absorbing the nitrous acid gas may not also absorb a portion of the residuary nitrous gas. *Nitrous acid* therefore is produced by the union of 300 measures of nitrous gas with 100 of oxygen; or (what amounts to the same) it consists of 150 measures of azote to 250 of oxygen. It is best made by dissolving nitrous acid gas in water, which becomes blue, green, and finally orange yellow, according to the strength of the acid and the quantity of gas absorbed. Hence it is that the orange yellow acid may be changed to the green, and the green to the blue, merely by proper dilution with water, which diminishes the relative strength of the acid in a given quantity.

The liquid nitrous acid is also made by passing nitrous acid gas into liquid *nitric acid*, which then becomes blue, green, or yellow orange, according to the concentration of the nitric acid.

M. Gay Lussac gives the following estimate of the composition of the oxyds of azote, viz.

Nitrous oxyd consists of 100 measures of azote with 50 measures of oxygen; or, by weight, of 63.72 of azote and 36.28 oxygen.

Nitrous gas consists of equal measures of azote and oxygen; or, by weight, of 46.757 of azote and 53.243 of oxygen.

Nitrous acid gas consists of 300 measures of nitrous gas to 100 measures of oxygen; or, by weight, of 34.507 of azote and 65.493 of oxygen.

Nitric acid consists of 100 measures of azote to 200 measures of oxygen, or of 200 measures of nitrous gas to 100. measures of oxygen; or, by weight, of 30.512 of azote to 69.488 of oxygen.

AZOTIZED OXYMURIATIC ACID, or AZOTIZED CHLORINE. (*Acide Murialeque azotée.*)

Under this term we shall describe a new and most remarkable compound of azote and oxy-muriatic acid, which appears to be the most violently detonating substance hitherto known. The first notice of the fact of this discovery published in this country is (we believe) con-

<sup>d</sup> Mem. d'Arcueil, tom. 2.

tained in the extract of a letter published by Sir H. Davy,<sup>a</sup> which announces the discovery of a compound of azote and chlorine appearing as an oil heavier than water, that detonates with all the violence of the fulminating metals by the mere heat of the hand, separating thereby in the gaseous form the two elements of which it is composed, evolving much heat and light. The writer also adds that this dangerous property had cost to the discoverer both an eye and a finger.

With this obscure hint of the nature of this substance, added to the recollection of the accidental formation of an oil by passing chlorine gas through nitrat of ammonia suggested by Mr. Children, Sir H. Davy has been enabled to produce this oily detonating compound, which indeed is a very simple process, and, as we are informed in the memoir on the subject, had nearly cost him the same unfortunate sacrifice of an eye as to the first discoverer (M. Dulong) in the attempt to become more familiar with the properties of this formidable compound.

M. Dulong has since made known all the particulars of this discovery in a paper lately read to the French Institute, of which a general abstract is given by Messrs. Thenard and Berthollet.<sup>b</sup>

From this and Sir H. Davy's memoir we learn the following particulars. Azote and oxymuriatic gas have no known action on each other when in the gaseous form, but when oxymuriatic gas is passed through a solution of the nitrat of ammonia, the oxalat, or many other ammoniacal salts, it is rapidly absorbed and a film collects on the surface, which is soon resolved into distinct drops of a yellowish oil that sinks to the bottom of the liquid, and is the detonating compound in question. A weak solution of pure ammonia will answer as well as the neu-

tral ammoniacal salt. A temperature of about 40° or 50° answers the best for its production. Sir H. Davy obtained it immediately by *shaking* in a phial a saturated solution of nitrated ammonia with about six cubic inches of chlorine, a mode of operating which appears attended with extreme hazard, for even when a large quantity of the gas was merely passed through a Woulfe's apparatus charged with the different ammoniacal solutions, the whole exploded violently and shattered the apparatus to pieces.

This detonating oil is yellowish, but quite transparent and highly liquid. Its smell is very nauseous, resembling that of the compound of carbonic oxyd and chlorine. It evaporates rapidly but silently when exposed to the air at a common temperature, but when slightly warmed it explodes vehemently, insomuch that it is dangerous to warm in any glass vessel a globule of the oil no bigger than a grain of mustard seed. When this oil merely touches many combustible matters, even without increasing the temperature, it explodes very violently, so as generally to shatter any glass vessel. This is the case when a globule of it is thrown into olive oil, turpentine, or naphtha. But with alcohol it only loses gradually its explosive property and becomes a white oily matter. When a particle of this oil touches phosphorus, or phosphorized alcohol and ether, it explodes with equal violence. It has no effect on muriatic or sulphuric acid, zinc, tin-foil or sulphur. M. Dulong attempted to analyze it by adding it, and the liquor in which it was formed, to a vessel containing copper filings. Muriated oxyd of copper was produced and azotic gas given out. It seems therefore to be without doubt a compound of chlorine and azote, but its unmanageable properties make its analysis an affair of difficulty and some danger.

## B

### BARIUM. BARYTES.

The basis of the earth barytes was first obtained by the eminent discoverer of the alkaline bases in the following way:° pure barytes was made into a paste with water, and a small cavity made in it to receive a globule of mercury, the barytes was laid on a slip of platina which was made positive in a voltaic battery, and the globule of mercury was rendered negative. In this state the barytes was deprived of oxygen, and its base, *Barium*, was obtained amalgamated with the mercury, from which it was separated

by evaporating the mercury. Barium thus procured is of a dark grey colour, with a low metallic lustre, and heavier than sulphuric acid. When thrown into water it effervesces, hydrogen is given off from one portion of the decomposed water whilst its oxygen unites with the barium, and barytes is reproduced and dissolves in the water.

Sir H. Davy estimates the elements of barytes to be about 89.7 per cent. of barium, and 10.3 of oxygen.

*Barytes* is the first oxyd of barium. Its

<sup>a</sup> Phil. Trans. for 1813.

<sup>b</sup> Ann. de Chim. tom. lxxxvi. p. 37.

<sup>c</sup> Davy's Elements.

properties have been fully described in our original article, and the difference between the pure barytes obtained from the nitrat and that procured from the crystals of barytes formed by solution in water, has been mentioned in the article *Alkali* in this appendix.

*Peroxyd of Barium.* According to the experiments of Messrs. Gay Lussac and Thenard, barytes can absorb oxygen, and thus produce an oxyd of barium of a higher state of oxydation than barytes.\* For this purpose some dry oxygen gas was passed into a glass tube over mercury, and along with it some fragments of pure barytes arising from the calcined nitrat. On applying the heat of a lamp, the oxygen was very rapidly absorbed, and the barytes appeared as if glazed on its surface, and became greyer.

The glass was then filled with hydrogen and heated as before. The hydrogen was absorbed in large quantity, and sparks were seen to proceed from the barytes. No water was vaporized, so that all of this fluid, which must have been produced by this absorption of hydrogen, was absorbed by the barytes, which then became very fusible.

The experiment was repeated with similar success with barytes prepared by calcining the carbonat of barytes with lamp-black in an intense heat; so that the effect could not have been produced in the first instance by any undecomposed nitric acid.

BENZONIN. BENZOIC ACID. BENZOATS.

We have to mention some additional facts relative to this resin and its products, which are among the most interesting of this class of vegetable substances.\*

When benzoin is gradually heated in moderately dilute nitric acid, it is dissolved into a light yellow liquid, which on cooling gradually deposits nearly the whole of the benzoic acid, whilst the resin appears to remain dissolved. This solution is totally decomposed by water.

Sulphuric acid dissolves benzoin into a deep red liquid, but carbonizes a portion of it. The solution gives a lilac precipitate with water. Acetic acid dissolves this resin even in the cold. When saturated by boiling, much benzoic acid separates on cooling.

When these acids are added to the solution of benzoin in alcohol, a precipitate is formed (with all but the nitric) which is probably a compound of the resin and acid, and an excess of the same acid generally redissolves a part of this precipitate. Nitric acid on the other hand does

not render the alcoholic solution turbid, but gives it a dark red colour, so that this acid seems to have a greater solvent power over the resin of benzoin.

*Benzoic Acid.* Scarcely two thirds of the whole acid contained in benzoin is procured by mere sublimation. Scheele's process (mentioned in our original article) gives the purest acid.

Some German chemists have also employed carbonat of potash or soda, as an intermede for obtaining this acid. Benzoin, boiled repeatedly with about a tenth of its weight of carbonat of soda and sufficient water, the resin being taken out two or three times and triturated, and again boiled with the same liquor, yields at last nearly the whole of its acid to the soda, and the solution of benzoat of soda deposits its acid on adding the sulphuric acid.

Benzoic acid is soluble in most of the acids, but separable from them by dilution with water.

A singular fluid compound of benzoic acid and camphor is mentioned by Mr. Gowar,<sup>b</sup> to be produced by adding a definite quantity of water to a solution of both these substances in alcohol.

Twenty grains of benzoic acid and as much camphor dissolved in half an ounce of common alcohol, and then diluted with as much water, gradually separates into two liquids, both of which are quite transparent if the acid is free from resin, but yellowish if otherwise.

Both the upper and lower liquids appear to be compounds of alcohol, water, benzoic acid and camphor. The lower, which has an oily appearance, is strongly acid and aromatic, and by evaporation forms crystals apparently composed of benzoic acid and camphor. Cold water added to this liquid immediately decomposes it, the benzoic acid being precipitated in the form of shining crystals, and the camphor floating on the top. The upper fluid on standing for a time, sometimes deposits large crystals floating upon the lower stratum, which are chiefly benzoic acid, but altered from its usual crystallized form, probably by the presence of some camphor.

It requires pretty exactly the above mentioned proportion of benzoic acid, camphor, alcohol and water, to produce this singular separation into two distinct solutions, for when more of the spirituous menstruum is used, the whole remains as one uniform solution, and when a greater proportion of water is employed, much of the camphor and part of the acid separate.

Mr. Bucholz has examined some of the leading properties of the benzoic acid, with a view

\* Recherches, tom. 1. p. 169.

<sup>a</sup> Brande in *Phil. Journ.* vol. 1.

<sup>b</sup> *Phil. Journ.* vol. xviii. p. 28.

of comparing them with the camphoric acid, some chemists having considered these two acids as nearly identical. The properties of the *Camphoric Acid* will be given under that article; those of the benzoic are the following:

Ten grains of benzoic acid were mixed with 500 grains of distilled water, and shaken in a phial for half an hour. The whole liquid was passed through a filter, the weight of which when dry was previously known, and after again drying there was found an addition of  $7\frac{1}{2}$  grains of weight produced by the undissolved acid. Hence Benzoic acid requires 200 times its weight of cold water for perfect solution. On the other hand it requires only 24 parts of boiling water, so that by far the greater part of the acid must again separate on cooling.

An hundred grains of cold alcohol dissolve by agitation about 56 grains of benzoic acid; and boiling alcohol dissolves nearly its own weight of the acid.

*Benzoat of Lime.* Benzoic acid boiled with carbonat of lime and water is gradually neutralized; and 50 grains of the acid require in this way about 20 grains of the calcareous earth, the pure lime of which is about 13 grains. The solution when much reduced by evaporation gives on cooling a number of shining silky needled crystals, often radiating from a common center; their taste is sweetish and somewhat earthy.

Though this benzoat of lime is prepared with the purest acid, and is perfectly white, when heated by itself in a close vessel it gives a liquid empyreumatic oil, smelling of the resin of benzoin. Benzoat of lime requires 20 times its weight of cold water for perfect solution.

*Benzoat of Potash.* This salt crystallizes when the acid is slightly in excess, forming small needles which require ten parts of cold water for solution. The neutralized salt is much more soluble and deliquescent.

It is to be observed that when most of the neutral benzoats are evaporated, part of the acid flies off, leaving the salt with a slight excess of base. This however is not the case with the benzoat of ammonia, the alkali being full as volatile as the acid. This property is of some importance as it gives a reason for a preference of the benzoat of ammonia in a very important use in analytical chemistry, to which it has lately been applied by Professor Berzelius.

This eminent chemist has found that the benzoic acid may be applied to the separation of iron from manganese, with equal success with the *Succinic*, and it has the advantage of being

much cheaper and more easily obtained. It is necessary for this purpose that the solution containing the mixed oxyds should be previously neutralized with accuracy, and then the benzoat of ammonia may be added as long as any precipitate falls down. This precipitate is merely benzoat of iron, and all the manganese remains in solution.

Not only will this salt separate iron from manganese, but as M. Hisinger has observed, it will equally separate it from all earthy salts, and from nickel, cobalt and many other metals, none of which are precipitated by the benzoat when properly applied.

(This will be further described in this appendix under the article IRON.)

#### BILDSTEIN.

From a recent analysis of this substance by Vauquelin,\* it appears to be composed of

- 56. Silex
- 29. Alumine
- 2. Lime
- 7. Potash
- 1. Oxide of Iron
- 5. Water

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100

It is interesting to observe, that in this mineral the character of unctuousity is by no means indicative of the presence of magnesia. The analogy also, as to chemical composition, between bildstein, mica, and felspar, is deserving of notice.

#### BILE.

This important fluid has been analyzed by Thenard,<sup>a</sup> a very skilful chemist, who has discovered in the bile of some animals what he considers as a new animal principle, to which he gives the name of *Picromel*, on account of its sweet and pungent taste.

The experiments on ox-gall are the following. A quantity of it was distilled to dryness in a retort, by which it lost from  $\frac{7}{8}$  to  $\frac{8}{9}$  of its weight of mere water a little flavoured. The dry yellow residue was calcined carefully in a platina or silver crucible kept scarcely at a cherry-red, by which it gave 22 per cent. of carbonaceous residue containing soda, common salt, phosphat and sulphat of soda, and phosphat of lime.

The uncombined soda amounted to no more than  $\frac{1}{200}$  of the original gall, which appeared much too small a quantity to be the intermede whereby the resin of this bile might be held in solution. Neither is the precipitate formed by acids at all equal to the whole of the solid

\* Journ. des Mines. No. lxxxviii. p. 247.

<sup>a</sup> Mem. d'Arceuil, tom. i.

matter which may be extracted from the bile, which is another reason for supposing some other substance besides soda which holds the resinous matter of bile in perfect solution. The analysis of ox-gall was thus conducted: A little nitric acid was first added, which precipitated a peculiar yellow matter along with a very little resin, which last was afterwards obtained pure by alcohol. The gall was filtered, and into it was poured a solution of sub-acetite of lead (made with 8 parts of common acetite and one of litharge) by which an insoluble compound of oxyd of lead and the resin of the gall fell down, (separable from each other by weak nitric acid) and the supernatant liquor was freed from the excess of the salt of lead by a current of sulphuretted hydrogen. The clear filtered liquor was evaporated to dryness, and gave the *Picromel* mixed with acetite of soda. The distinguishing properties of picromel, according to M. Thenard, are its pungent sweetish taste, and the great solvent power which it exercises over the resin of the bile; so that by adding again the due proportions of this resin, of picromel, of the yellow matter separable by nitric acid, and of soda, the author obtained an uniform liquid exactly resembling the original bile from which these substances had been extracted. Of 800 parts of ox-gall the author finds 700 of water, 24 of resin, 60½ of picromel, about 4 of yellow matter, and 4 of soda, and the rest salts of soda and lime.

Picromel dissolves both in water and in alcohol, does not crystallize, and forms a triple compound with resin and soda, highly soluble in water, and not decomposable by acids, alkalies, and earthy salts; but it is separated by some metallic salts.

The resin of bile is green, bitter, soluble in alcohol, and separable thence by water, and soluble in alkalies, and in some acids, but not in all.

It appears however in the author's second memoir on this subject, that the picromel is not so certainly obtained in the above method; for he says that if too much of the acetite of lead is added, the picromel itself is separated, so that it is necessary to assay the precipitate from time to time, and as soon as it becomes totally soluble in weak nitric acid, it will shew that all the resin has been separated, and that the picromel itself begins to precipitate.

M. Thenard gives the result of the analysis of the bile of different animals, and finds no picromel in human bile, this secretion containing chiefly water, albumen, a peculiar resin, soda, and some salts.

Professor Berzelius in his analysis of bile,<sup>b</sup> entirely denies the existence of this peculiar substance, *picromel*, as a distinct animal principle, and seems to consider nearly the whole of the solid contents of the bile (the saline part excepted) as one peculiar albuminous substance, which partly precipitates in the form of a resin when some mineral acid is added; and therefore this supposed resin is a compound of the peculiar bitter albumen of bile with a small portion of the acid employed. This biliary matter is soluble in water, even without the assistance of alkali or of any other intermede; and it forms two compounds with some acids, one soluble, the other not so, and therefore precipitated, and in the form of a resin. But the acetous acid which gives soluble compounds with the albumen of blood does the same with biliary albumen, and hence no precipitate follows the addition of this acid to bile.

The biliary matter may be obtained pure in the following way: mix fresh bile with sulphuric acid diluted with 3 or 4 parts of water, a yellow precipitate whose nature is hardly known first appears and must be separated; then continue adding more of the acid as long as any thing falls down, decant the fluid part and edulcorate the remaining green resiniform substance. This, which is in fact a compound of biliary albumen and sulphuric acid, may be deprived of its acid either by digestion with carbonat of barytes and water, or by solution in alcohol, and digesting the liquid with carbonat of lime as long as it reddens litmus. The clear liquor then contains the pure biliary albumen, which is to be evaporated to dryness. This gives a green solution in water closely resembling the natural bile. The quantity of this biliary matter he estimates at  $\frac{8}{100}$  of the whole bile.

#### BIRDLIME.

This substance has been commonly supposed to be analogous to vegetable gluten, like that of wheat, but it does not appear to have been analyzed with any care till Bouillon la Grange examined it, and he has found the following properties.<sup>a</sup>

The birdlime here employed was that of the inner bark of the holly, prepared by bruising the bark in a mortar, boiling it with water for four or five hours, throwing away the liquor, and putting the residue in earthen pots, and keeping it in a damp cellar till it was mouldy and viscous, moistening it now and then with water, and then washing it thoroughly with water to remove all heterogeneous matters.

<sup>b</sup> Medico-Chirurg. Transact. vol. iii.

<sup>a</sup> Ann. Chim. tom. lvi.

Birdlime thus prepared is greenish, bitter, very tenacious, spinning out into threads when drawn asunder, and smelling somewhat like linseed oil. When a thin layer is spread out on glass and exposed for some time to light and air it dries, turns brown, and is then no longer viscous, even when again wetted, but may be ground to powder. It reddens litmus. When birdlime is heated without addition, it melts into a pasty mass, swells, becomes full of bubbles, smelling like heated oil, and if put upon heated coals, or when red hot, it burns with much flame and dense black smoke. It continues to burn when once lit, till it is entirely reduced to an ash, which is white and very alkaline.

Water boiled upon birdlime has little or no action upon it except to render it rather more fluid, and to dissolve out a portion of acid (which is shewn by the water reddening litmus) and a little mucilage and extract.

But caustic potash acts very powerfully upon birdlime. A strong lye of potash boiled with birdlime forms a white magma which on evaporation turns brown, hardens, and acquires the smell and taste of soap. This soap dissolves in alcohol and water, and is decomposed by acids like the common soaps.

Sulphuric acid blackens and carbonizes birdlime, and on adding lime the smell of vinegar is perceived.

Nitric acid heated on birdlime converts it to a hard brittle mass, which when treated with more of the same acid, is partly changed to oxalic and malic acid, and partly to a yellow wax-like resin, soluble in potash and in alcohol.

Birdlime long shaken in concentrated oxymuriatic acid becomes white, loses its viscosity and is broken into hard compact masses, still enclosing a portion of the unchanged birdlime.

Acetous acid softens birdlime and dissolves a portion. Carbonat of potash does not disturb this solution, and when evaporated to dryness it leaves a residue resembling the resins, but which cannot be perfectly dried.

Boiling alcohol dissolves birdlime. The solution is of a clear yellow when hot, but becomes turbid on cooling, and deposits a yellow matter like wax, whilst the clear liquor remains bitter, nauseous, acid, and leaves a kind of resin when evaporated.

Sulphuric ether totally dissolves birdlime, and with more ease than any other reagent. The solution is greenish, yellow and acid. When much water is added, an oil separates and comes up to the surface, which much resembles linseed oil, and will form a compound like plaster when boiled with litharge. The ethereal solu-

tion of birdlime when evaporated leaves a yellow soft matter like wax. All these facts shew the analogy of birdlime with oily or resinous substances, and its entire difference from vegetable gluten.

#### BISMUTH.

1. Native. Its primitive form, according to Haüy is the regular octohedron; and the only other crystal that he mentions as belonging to this species, is an acute rhomboid, the alternate angles of which are 60° and 120°.

Besides the three species of ores described in the article Bismuth in this Dictionary, there are certain natural mixtures probably, rather than combinations, of metals in which bismuth is the predominating ingredient, and which therefore may be mentioned here.

#### 1. Bismuth with Copper and Sulphur.

This substance was discovered by Selb in the cobalt mine of Neugluck, in the district of Furstenberg. Its colour is steel-grey, by exposure to the air becoming bluish and reddish; has a slightly metallic lustre, a fine grained fracture, is soft and semi-ductile. According to Klaproth, it is composed of

47.24	Bismuth
34.66	Copper
12.58	Sulphur

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94.48

#### 2. Argentiferous Bismuth.

Its colour is a pale lead-grey becoming darker on exposure to the air; it is generally disseminated, rarely in mass. It melts easily before the blowpipe. It occurs at Schatzlach, in the Black forest, and according to Klaproth, is composed of the following ingredients.

33.	Lead
27.	Bismuth
15.	Silver
4.3	Iron
0.9	Copper
16.3	Sulphur

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96.5

#### 3. Nadelierz.

Its colour is steel grey verging more or less to copper red, but generally is dull, and superficially yellow or green from decomposition. It occurs disseminated, or crystallized in striated acicular hexahedral prisms, often curved, sometimes articulated, and always implanted. Its longitudinal fracture is lamellar with a splendid metallic lustre. It is soft, semiductile, and its specific gr. is about 6.1. It occurs in Siberia in white quartz mixed with native gold.



It has been analyzed by M. John, and appears to consist of

43.2	Bismuth
24.32	Lead
12.1	Copper
1.58	Nickel
1.32	Tellurium
11.58	Sulphur
<hr/>	
94.1	

Pr. Berzelius<sup>a</sup> states the composition of the oxyd of bismuth from the very accurate experiments of M. Larserhjelm, to be

Bismuth	. 90.803	—	100.00
Oxygen	. 9.197	—	10.13
<hr/>			<hr/>
	100.000		110.13

*Sub-sulphat of Bismuth.* Some of this salt was prepared by decomposing the neutral sulphat by water. The sub-sulphat, thus precipitated, being washed and dried on very hot sand, 100 parts of the dried salt were strongly ignited in a platina crucible till no further loss of weight was perceived. The loss was 14.5 and consisted of sulphureous acid and oxygen, leaving 85.5 of oxyd of bismuth. The 14.5 sulphuric acid thus decomposed, and the 85.5 of oxyd each contain 8.66 parts of oxygen.

The *Neutral Sulphat of Bismuth* is composed of so much acid as contains three times as much oxygen as that of the base with which it is saturated. This would give the elements of this salt to be 14.5 sulphuric acid and  $\frac{85.5}{3} = 28.5$  oxyd, or

Sulphuric Acid	. . . 33.7
Oxyd of Bismuth	. . . 66.3
<hr/>	
	100.0

*Nitrat of Bismuth.* 10 parts of this salt, crystallized, reduced to powder, and dried in the air, were distilled in a small retort. The nitrous acid that passed over was colourless and not fuming, which shews the presence of much water of crystallization. In the retort were left 4.88 parts of oxyd, so that the crystallized nitrat well dried contains

Nitric acid and water	. . . 51.2
Oxyd of bismuth	. . . 48.8
<hr/>	
	100.0

*Sulphuret of Bismuth.* This compound

<sup>a</sup> Ann. Chim. tom. 82. p. 121 and 241.

consists, according to Vauquelin, of 68.25 of bismuth, and 31.75 sulphur, as mentioned in the article *Sulphuret* in this appendix.

**BITTERSPTH, or MAGNESIAN CARBONATE OF LIME.**

The primitive crystalline form of this substance is considered by M. Haüy as precisely the same with that of calcareous spar; hence he considers the magnesia contained in it as purely accidental, and on this account denominates it *Chaux carbonatée magnésifère*. Dr. Wollaston however has shown that the obtuse angle in the primitive rhomboid of calcareous spar measures  $103^{\circ}.5'$ , while the same in the primitive rhomboid of bitterspath is at least  $106^{\circ}.15'$ . The two substances may therefore be regarded as specifically distinct.

**BLOOD.**

Several very important additions have been made to the chemical knowledge of this most interesting of all the animal fluids. We shall give a short abstract of them.

It was stated as a discovery of Fourcroy and Vauquelin, and confirmed by Parmentier and Deyeux, that the serum contains *Gelatine*, and the particulars were mentioned under the article **BLOOD**, (*Ch. Dict. vol. 1.*) It has since been very amply proved however that this is a mistake, and that the substance contained in serum, uncoagulated by heat, is not gelatine, though on evaporation to dryness it leaves a stiff transparent mass. Dr. Bostock, who first detected the mistake of these eminent chemists on this subject, has the following remarks.<sup>b</sup>

He defines *Gelatine* or *Jelly* to be an animal substance which is liquefied by heat, becomes concrete by cold, and with tan forms a compound insoluble in water. After the serum has been partially coagulated by heat, the liquid that remains, (or the *Serosity*,) yields a sensible precipitate when heated with corrosive sublimate, shewing the presence of some albumen which has escaped the first coagulation by heat, after which the liquid may be evaporated nearly to dryness without shewing any degree of gelatinization on cooling, and without being at all altered by infusion of tan; both of which circumstances prove the absence of gelatine. This was further shewn by the addition of a small portion of gelatine to the serosity, which now gave all the characters belonging to this animal principle. Dr. B. however does not consider the whole of the animal matter in the serosity to be albumen that has escaped coagulation, but supposes a

<sup>b</sup> Medico-Chirurgical Transact. vol. i. and ii.

portion to be similar to animal *mucus*, though its nature is obscure. This matter forms about 2 per cent. of the serosity, and the remaining solid contents amount to about 10 per cent. more.

Dr. Marcet<sup>c</sup> has given some valuable experiments on the contents of the serosity as compared with those of other watery fluids of the animal body, whether natural or morbid. The specific gravity of serum varies remarkably, being found from 1024.5 to 1032.5. On a careful analysis he gives the following as the constituent parts of serum, the dry contents being all thoroughly desiccated in a sand heat without charring or decomposition :

Water . . . . .	900.00
Albumen . . . . .	86.80
Muco-extractive matter . . . . .	4.00
Muriat of soda with a little muriat of potash . . . . .	6.60
Sub-carbonat of soda . . . . .	1.65
Sulphat of potash . . . . .	0.35
Phosphats of lime, iron, and magnesia . . . . .	0.60
	<hr/>
	1000.00

It will be seen therefore that serum contains a tenth of its weight of solid contents, nine-tenths of which are animal matter, and the rest saline.

Dr. M. agrees with Dr. Bostock in asserting the total absence of true gelatine in serum, but allows a kind of muco-extractive matter, which is distinguished by being incoagulable, and soluble in water and other menstrua. The little albumen with which it remains combined after the serum has been heated is entirely separable by being boiled with corrosive sublimate.

Since the publication of Dr. Bostock's paper Mr. W. Brande has made some chemical researches on the blood,<sup>d</sup> in which he has very happily applied the galvanic influence, in order to detect the real nature of the animal matter that remains in serosity after the coagulation of the bulk of the albumen by a boiling heat. One ounce of pure serum was diluted with water, the conductors from a battery of thirty pairs of four inch plates were immersed in this solution at a distance of two inches from each other, and the whole of the albumen coagulated in contact with the negative wire in three hours and a half, the coagulum being occasionally removed. A similar effect was produced in the serosity after the greater part

of the albumen had been coagulated by heat; the fluid was then exposed to the galvanic action, and albumen coagulated at the negative wire. In both cases the fluid, evaporated after the galvanic action was over, gave no change on adding infusion of galls, nor afforded any gelatine when dry. On the other hand, some solution of isinglass was added to serum, and the galvanic action applied, but after all coagulation had ceased, the liquid still gave a copious precipitate by galls. Hence it appears that galvanic electricity has no effect in separating gelatine from its solution, though it totally precipitates albumen. It was also found that heating serum with the addition of a little muriatic acid, as effectually coagulates the whole of the albumen as is done by the agency of galvanism.

Mr. Brande has given some additional facts relative to the properties of the colouring matter of the blood, which (as well as those of professor Berzelius, to be presently mentioned) throw much uncertainty on the hypothesis of Fourcroy and Vauquelin, that the colour is given by a sub-phosphat of iron dissolved in serum, and indeed make it doubtful whether this metal is at all concerned in giving to blood its deep and beautiful colour. The colouring matter was generally obtained by stirring venous blood with a stick as soon as drawn; the fibrin collects at the end of the stick, and the colouring matter is diffused through the serum, from which it gradually subsides, and may therefore be collected in a very condensed form though still mixed with serum. This substance readily dissolves in water, making a bright red solution when filtrated, which however becomes brown and separates by a boiling heat into a clear colourless water and a brown sediment. Muriatic acid, poured upon the dense colouring matter above described, renders one portion brown and insoluble, but dissolves the other portion into a liquid, which when filtrated is a dark crimson in reflected light, but greenish in transmitted light. The colour is not altered by long exposure to light, nor by a boiling heat, nor materially by alkalies, nor by galls. The dilute sulphuric acid extracts the colouring matter as well as the muriatic. Both these solutions may also be made by digesting at a heat of 150° to 200° some pieces of the common coagulum of blood with the acid employed. If muriatic acid, it may be diluted with an equal quantity of water; and if sulphuric,

<sup>c</sup> Medico-Chirurgical Transactions. vol. 2.

<sup>d</sup> Phil. Trans. for 1812.

with eight or ten parts of water. The nitric acid on the other hand much impairs the fine colour and gives it a shade of brown. The acetic acid acts as the muriatic, but with still more distinction between the effect of reflected and transmitted light. With the tartaric acid the solution inclines to scarlet.

Both the caustic and carbonated alkalies form deep red solutions of this colouring matter, which are very permanent. Soda gives a colour more inclining to a crimson, and ammonia still more. When these solutions are supersaturated with nitric acid the colour passes into bright yellow.

The author then endeavoured to combine this colour with some of the common mordants. Alumine would not answer, for though it extracted the colour pretty well, it became brown instead of retaining its original red. The solutions of tin succeeded scarcely better. Those of mercury answered the best. When corrosive sublimate is added to the aqueous solution of the condensed colouring matter, its tint is instantly brightened, and it becomes slightly turbid from the deposition of a little albumen. If this be immediately filtered, the clear liquor gradually deposits a deep red insoluble precipitate which carries down the whole of the colour. Woollen cloth first steeped in corrosive sublimate and then in a watery solution of the colouring matter of blood, acquires a permanent red tinge unalterable by soap, which possibly may be of use in dyeing.

We shall conclude this article with a very short abstract of the most original parts, in an elaborate analysis of blood made by professor Berzelius, being one of a series of investigations on animal fluids, first published in this country in the *Medico-Chirurgical Transactions*, vol. 3.

The blood selected for experiment was that of the ox.

Blood, he observes, may be regarded as a liquid holding a colouring matter suspended in it, but not dissolved.

The only practicable way of separating the constituent parts of blood is that of coagulation, as usually employed, though this is imperfect, as much of the serum remains attached to the red globule in the coagulum.

The crassamentum contains the fibrin and the colouring matter, which are separable by washing, in the way often described.

*Fibrin.* No part of this is soluble in cold water, but a portion is extracted by long boiling, which when the liquor is evaporated

gives a white, dry, friable residue, soluble in cold water, and of an agreeable taste like broth. Fibrin, when long boiled, loses the property of being soluble in acetic acid.

Alcohol digested with fibrin changes it to an adipoceros or fatty matter, soluble in the alcohol, and separable by water. This fatty matter is formed in the process, and does not exist as such in the recent fibrin.

Ether has a similar effect with alcohol, and the fatty matter is more abundant and more nauseous.

Concentrated acetic acid immediately softens fibrin, renders it transparent, and when heated dissolves it into a tremulous jelly, which is soluble in warm water. When this solution is evaporated to dryness it retains sufficient acid to redden litmus, but will not redissolve without more acid. Sulphuric, nitric, and muriatic acids, give a precipitate with this solution composed of fibrin and the acid employed, which when washed with water loses a part of the acid, and the remainder dissolves in more water. More acid will again give a precipitate with the latter solution, so that fibrin with a certain portion of acid is soluble in water, and with an excess of the same acid becomes insoluble. Alkalies also give a precipitate with the solution of fibrin in acids, and an excess of alkali redissolves it.

Weak muriatic acid, digested with fibrin, hardens and shrinks it, and long boiling with water at last converts this to a soluble gelatinous mass. Some azotic gas is given out. This solution is again precipitated by an excess of the acid.

Concentrated muriatic acid decomposes fibrin when boiled upon it, and gives a violet coloured solution.

Sulphuric acid, when diluted, has a similar effect on fibrin with muriatic acid; and like this, produces two compounds with it, one insoluble, in which the acid is in excess; and the other, where the acid is scarcely predominant, soluble in water. Nitric acid of 1.25 sp. gr. digested with fibrin turns it yellow; and forms a small quantity of fat on the surface. Pure azotic gas is given out. After a day's digestion the fibrin becomes a yellow powder, which turns to orange by washing, and is less acid, but still remains enough to redden litmus. This substance, first discovered by Fourcroy and Vauquelin, was supposed by them to be a new acid, and called by them *Acide Jaune*, but professor Berzelius considers it as a compound of fibrin, with nitric or nitrous

acid, and with the *malic* acid formed by the action of the nitric acid on the fibrin. The latter acid is thus detected: the yellow powder above mentioned is first boiled with alcohol, which when cool deposits an adipoceros matter, that is to be removed. The liquor is then digested with water and chalk, which slowly dissolves the earth with some effervescence, and this solution, made clear by filtration, is evaporated to a syrupy consistence, and then mixed with alcohol, which dissolves one part and precipitates another. The precipitate has all the characters of *malat of lime*. The part dissolved in the alcohol is nitrat of lime.

Caustic alkali first enlarges, then dissolves fibrin forming a yellowish green liquor. The fibrin is somewhat changed by this process, for acetic acid which separates it from the alkaline solution will now no longer redissolve it. But nothing like a true soap is produced by the action of alkali on fibrin.

*The Colouring Matter.* To obtain this in tolerable purity the crassamentum of blood was cut into thin slices, and dried on sheets of blotting paper. This was rubbed with water which extracted so much as to acquire a very deep brown colour. This solution was coagulated by heat, forming a dark brown matter which when dried under a press was a black hard substance, with a vitreous fracture, and was considered as the colouring matter.

The properties of this matter are so nearly the same as those of fibrin that we shall not enumerate them. They are distinguished chiefly by the difference in colour, and by the fibrin coagulating spontaneously as soon as drawn, whereas the colouring matter requires to be heated. Albumen has the same general properties and habitudes with acids, so that the greatest chemical difference between fibrin, albumen, and colouring matter, consists in the colour of the latter, and this leads to the still problematical question as to the *cause of the Colour of the Blood*.

The author asserts (contrary however to the experiments of some chemists) that oxyd of iron, which is found in a notable quantity in the ashes of the colouring matter, is not contained (or at least only in an infinitely small portion) in the ashes of fibrin or albumen.

We have already stated in our former article the opinion of Fourcroy and Vauquelin on the mode in which the iron that they suppose colours the blood exists in that fluid, being a red sub-phosphat dissolved in albumen. Parmentier and Deyeux suppose that the naked

alkali of blood is the great agent that holds in solution this colouring metal. But our author conceives that all are mistaken, and that the mode in which the iron is combined, is totally unknown, though he attributes the colour to the presence of this metal, but not as an oxyd united to any acid.

By incineration of 20 grammes of colouring matter till the charcoal was completely destroyed, he obtained 0.25 gramme of a yellowish-red ash. 100 parts of this ash accurately analyzed, gave the following results, viz.

Oxyd of iron . . . . .	50.0
Sub-phosphat of iron . . . . .	7.5
Phosphat of lime with a little magnesia . . . . .	6.0
Pure lime . . . . .	20.0
Carbonic acid and loss . . . . .	16.5
	<hr/>
	100.0

But the phosphat of iron was probably not contained as such in the colouring matter, but was produced by the process of the analysis. The chief arguments which the author brings against Messrs. Fourcroy and Vauquelin's hypothesis, are the want of any precipitate when the prussiates, gallic acid, barytic water, phosphoric acid, and sulphuret of potash are added to the colouring matter, all of which would act differently on any solution of a *salt* of iron, such as the sub-phosphat is. He also shews (and this is in direct opposition to the above French chemists) that the sub-phosphat artificially prepared and mixed with serum, does *not* produce any thing at all resembling the colouring matter of blood, but only a rusty coloured liquid, from which the colouring matter may be totally separated by mere filtration. It is true that many of the oxyds of iron are largely soluble in serum, but these solutions easily shew the presence of this metal with those tests that fail to discover it in the blood itself. The prussiates alone do not disturb the solution of iron in albumen, as the solvent of the metal is not an acid.

*Of the Serum, Albumen, and Salts of the Blood.*

The chemical properties of albumen are so nearly the same as those of fibrin, that the same description will serve for both. The ash of burnt albumen is white and perfectly free from iron. It chiefly consists of phosphat and carbonat of lime, with a little magnesia.

Human blood differs but little from that of the ox in its chemical analysis. The serum of

human blood is thus composed according to our author, viz.

Water . . . . .	905.0
Albumen . . . . .	80.0
Substances soluble in alcohol, viz.	
Muriat of potash and soda . . 6.	} 10.0
Lactate of soda with animal matter 4.	
Substances soluble only in water, viz.	
Soda, phosphat of soda, and a little animal matter	} 4.1
	999.1

This analysis has a very satisfactory agreement with that of Dr. Marcet just stated, considering the varying nature of the blood and the difficulties of analysis. There is one substance however now for the first time introduced by Professor Berzelius as a component part of this, and indeed of most other animal fluids, which is the *Lactate of Soda*.

The *Lactic Acid* was first discovered by Scheele, and by him was considered as having sufficiently distinct properties to be entitled to a place among the list of particular acids. Latterly however some eminent French chemists have sought to prove that the supposed Lactic acid is only a combination of acetous acid with some animal matter. But it appears that the only proof of the identity of this with the acetous acid has been the production of vinegar when the lactic acid is distilled with the sulphuric, in which case there condenses in the receiver a mixture of sulphureous and empyreumatic acetous acid, from which the latter is obtained pure by subsequent rectification. To this Pr. Berzelius objects that by a parity of reasoning all the vegetable acids hitherto considered as distinct species might be reckoned as acetous, modified by some peculiar substance, since they all yield acetous acid when distilled with the sulphuric.

Many chemists, he observes, have noticed in their analysis of animal fluids that the alcoholic solution when evaporated leaves a yellow deliquescent-extractive mass. This contains *Lactate of Soda* and an animal matter which always accompanies it, but may be separated by tannin. To analyze it, dissolve the whole in alcohol, add a mixture of sulphuric acid diluted with much alcohol as long as there appears any precipitate, which is sulphat of soda. Digest the spirituous solution (which often contains the sulphuric, muriatic, lactic and phosphoric acids)

with carbonat of lead, and all these acids will unite with the oxyd of lead; but of these the lactate alone will be soluble in alcohol which is therefore to be added. Then decant the alcoholic solution, separate the lead by a current of sulphuretted hydrogen gas, and the clear liquor will contain the lactic acid. This may be further evaporated, but cannot be crystallized.

#### BORACITE.

The primitive form of this substance is a cube; and it is remarkable that in the secondary crystals those parts which correspond to the opposite solid angles of the primitive nucleus are destitute of that symmetry which prevails in most crystalline bodies; in this respect however they are analogous to the secondary crystals of tourmaline, and, like these, are electric by heat, and exhibit on the opposite dissimilar faces, at one extremity positive, and at the other negative electricity.

#### BORACIC ACID. BORACIUM.

The powerful deoxygenating energy of Potassium has been very successfully applied to the discovery of the basis of the boracic acid, the decomposition of which had frequently been attempted before without success. The fact of the production of a new olive coloured substance from boracic acid on the negative surface of a powerful galvanic pile was indeed the first approach to the knowledge of the base of this acid made by Sir H. Davy; and the same chemist some time after announced the production of a black substance, on igniting boracic acid in a gold tube with potassium.<sup>b</sup> Since this time more numerous and very similar experiments were carried on nearly at the same period both in this country and by Messrs. Gay Lussac and Thenard,<sup>c</sup> from which the following properties have been made out of the base of this acid, to which the French chemists have given the name of *Bore*, and Sir H. Davy, *Boracium*.

Boracium is thus prepared. Take some pure boracic acid, which is done by decomposing borax, either by sulphuric or muriatic acid, but if the sulphuric is used, the precipitated boracic acid must be fused for a few minutes in a Hessian crucible to expell some of the sulphuric acid that adheres to it. A platina crucible will not answer, as it would be soon spoilt by the operation. If muriatic acid is employed, the boracic is pure at first, and then crystallizes in very small scales, whereas when it contains a little of the sulphuric, the scales are much

<sup>a</sup> Phil. Trans. for 1808.

<sup>b</sup> Ibid for 1809.

<sup>c</sup> Recherches, tom. I.

larger and broader. Put equal parts of the boracic acid reduced to fine powder, and of potassium into a small tube either of coated glass or of brass, copper, or iron, and adapt a narrow glass tube dipping under mercury to keep out the external air. Then gradually heat the ingredients in a small furnace till the tube becomes of a low red, and keep it thus for a few minutes and the operation is finished. Scarcely any gas is expelled in the process, but as soon as the heat reaches a certain point, a vivid inflammation takes place, which melts the glass tube if more than a few grains of each material are used; so that on this account a copper tube is preferable. The product of this experiment is an olive-coloured earthy looking matter, which when boiled for a few minutes partly dissolves in water leaving behind a dark olive-coloured powder which should be welledulcorated with sufficient muriatic acid to neutralize the excess of alkali, and dried. The solution contains borat of potash and an excess of caustic potash; the olive powder is the *Boracium*. With equal parts of boracic acid and potassium there is always a great proportion of the acid undecomposed, for Sir H. Davy finds that 20 grains of potassium are required to decompose 8 grains of the acid, but no inconvenience arises from this deficiency of potassium besides the loss of a little boracic acid, as the boracium is completely separated by water from the potash and borat of potash.

Boracium is an opaque friable insipid powder, neither acid nor alkaline. It neither melts nor volatilizes when strongly heated in close vessels but only becomes denser. It is insoluble in water, alcohol, ether or oils. When it is gently heated in a retort filled with oxygen gas, it kindles and burns with most vivid scintillations and a brilliant light. A sublimate rises from it, which is boracic acid, and a coating of the same acid also vitrifies around the burning mass, which, after a while, extinguishes the combustion before the mass is entirely converted to acid; and hence it remains black, and only partly soluble in water, the insoluble portion being combustible as before. Boracium also burns in common air when heated red-hot, and the combustion is only partial for the same cause. When boracium is placed in contact with oxymuriatic gas at a common temperature, it instantly takes fire and burns with a brilliant white light, and a white sublimate coats the vessel, which when moistened yields boracic acid. When thrown into nitric acid, boracium renders it bright red, and when heated, there is much effervescence of nitrous gas, the boracium dis-

appears and the acid liquor contains boracic acid. Boracium heated with most neutral salts deprives their acids of the oxygen which they contain. Thus when calcined in close vessels with sulphat or sulphite of soda, borat of soda and sulphur are formed: when heated with nitre or oxymuriat of potash, much deflagration ensues, and borat of potash is produced. It also decomposes carbonat of soda in a high temperature, forming borat of soda and charcoal.

There is some difficulty in fixing with any accuracy the proportions of boracium and oxygen in boracic acid; for in any common mode of burning these two substances, the operator is obliged to interpose several lixiviations of the product on account of the imperfect combustion for the reason already described. The oxygenation by nitric acid answers better, for when boracium is boiled for some time in this acid, it is totally changed to boracic acid, the weight of which after boiling down and ignition indicates that this acid contains one third of oxygen and two-thirds of base. These proportions however, which are those of the French chemists, do not even approach to those of Sir H. Davy, who estimates about two parts of oxygen to one of base. As the olive-coloured substance obtained by potassium and boracic acid does not conduct electricity, and combines with alkalies, it is conjectured by this chemist to be not the pure base but a primary oxyd; and when some of it is heated strongly with potassium and iron filings, a dark metalline mass is formed which conducts electricity, slightly effervesces in water, and by solution in nitric acid gives oxyd of iron and boracic acid.

If this conjecture be well founded, there would appear to be three substances here concerned, namely: the base of boracic acid or *Boracium* which is still not known: the *Olive oxyd* above described and improperly called boracium; and the boracic acid. From some appearances in one of the experiments it appears also not improbable that there is a blackish oxyd containing more oxygen than the olive matter and intermediate therefore between this and boracic acid.

#### BRAUNSPATH.

This substance from the supposed identity of its primitive crystalline form is considered by Hauy as carbonate of lime, with a variable and accidental proportion of carbonate of iron, (*Chaux carbonatée ferifere*). But Dr. Wollaston has shown that the obtuse angle of its primitive rhomboid measures  $107^{\circ}.0'$ , instead of  $105^{\circ}.5'$  that of calcareous spar.

BRONZITE, see DIALLAGE.

## C

## CALCIUM. BASE OF LIME.

The same evidence for the existence of a Base of Lime is obtained both by analogy and by direct experiment as for the base of Barytes or Barium, and the mode of obtaining Calcium is the same as that described for *Barium*, substituting pure white marble or chalk to the carbonat of barytes. Calcium has been procured in such minute quantities that but little is known about it, except that is a bright white metal which produces lime when oxydated.<sup>a</sup>

Lime appears to consist of about 40 of calcium to 15 oxygen. When lime is moistened with water or slacked, and dried at a heat short of redness, it retains a portion of water and is then properly a hydrat of lime, and it consists of about 17 of water to 55 of lime. A red heat again expells all the water, so that lime does not retain water so obstinately as the fixed alkalies, which remain hydrats even when fused by themselves at a red heat.

## CAMPHOR. CAMPHORIC ACID.

M. Bucholz<sup>b</sup> has made several experiments on this acid, particularly with a view of comparing its properties with those of the benzoic acid.

He prepares this acid in the following way. Two ounces of camphor are mixed with a pound and a half of nitric acid of 1.25 sp. gr. and half a pound of the same acid of 1.55 sp. gr.: half the acid is distilled over with a gentle heat and then returned on the materials in the retort and again distilled as before, and this is repeated three times. After the second distillation no more of the camphor appears than a little oil of camphor floating on the acid. When the process is concluded, the camphoric acid is found above the acid in the form of a white butyraceous matter. This is separated from the acid by a glass funnel, and is further freed from the adhering acid by being dissolved in boiling water, when it crystallizes pure on cooling. From two ounces of camphor about five drams of the crystallized acid are obtained, besides a portion which may be washed away by the water employed to separate the adhering acid. Care must be taken not to urge the distillation of the nitric acid too quickly, as it would then decompose the camphor instead of acidifying it; and this is marked by a brown colour in the residue.

The camphoric acid separates from its so-

lution in hot water in feathery crystals like those of muriated ammonia.

Camphoric acid requires for its solution 100 parts of cold water, but only 11 parts of boiling water. It dissolves in its own weight of alcohol at a common temperature, but in every proportion when boiling, forming a liquid mass which solidifies on cooling, if the acid is in large proportion.

*Camphorat of Lime.* To 50 grains of camphoric acid in 3 ounces of water, carbonat of lime in powder was added gradually. The effervescence ceased when 30 grains of the carbonat had been added, but it still strongly reddened litmus, which shews the existence of a camphorat of lime with excess of acid. When this solution is saturated with lime and much reduced by evaporation, it crystallizes, but not in very defined crystals. The taste of this solution is neither salt nor bitter, but somewhat acerb, and leaving a taste of lime, so that this crystallized salt is probably with an excess of base. This salt requires only five parts of cold water to be dissolved.

*Camphorat of Potash.* When the saturated solution is brought to a syrupy consistence and left to evaporate spontaneously, small granular crystals are formed, which, when warmed, again liquefy.

In all the above described properties the camphoric acid differs very sensibly from the benzoic.

**CAMPHOR.** A singular combination of this substance and *Benzoic acid* is described under this latter article in the Appendix.

Some further observations on Kind's artificial camphor produced from muriatic acid and oil of turpentine have been made by Thenard.<sup>c</sup> The original experiments of Kind have been already described (*Chem. Dict. art. Camphor*) that of Thenard, which agrees most accurately with the other, is as follows: A hundred grammes of rectified oil of turpentine were put into a vessel surrounded with a freezing mixture of ice and salt, and muriatic acid gas introduced, of which 30 grammes were absorbed. No gas was given out except muriatic, when the oil of turpentine began to be saturated. The mixture assumed a soft consistence and became a crystalline mass; and after draining three days, 20 grammes of a liquid separated, leaving nearly 110 grammes of the peculiar white granulated

<sup>a</sup> Davy.

<sup>b</sup> Ann. Chim. tom. lxxxiv. p. 301.

<sup>c</sup> Mem. de Arcueil, tom. ii. p. 29.

substance, which is the *artificial camphor*. When this is washed by a weak alkaline solution, all acidity sensible to the taste and to test liquors is lost; yet when it is sublimed or passed through a red-hot earthen tube, much muriatic acid appears; and also when nitric acid is boiled upon it, much nitro-muriatic acid is given out. The fluid portion that drained from the mass had a similar composition and contained much muriatic acid. These drainings are black if common oil of turpentine be used.

With regard to the nature of this singular substance M. Thenard denies the probability of any decomposition of the oil, but considers it as a mere compound of muriatic acid and oil, in which the union is so intimate, that all the sensible properties of an acid are lost.

**CANTHARIDES. SPANISH FLY.** The well known acrimony of this insect shewn in its powerful blistering quality, has often made it the subject of chemical examination, chiefly with a view of separating the principle in which this acrimony resides. M. Robiquet<sup>a</sup> gives the following method of obtaining it. Boil any quantity of bruised cantharides in distilled water, strain off the reddish-brown decoction, and add more water to the residue to extract all that is soluble. Mix and evaporate all the decoctions in a moderate heat to the consistence of a soft extract, and digest this repeatedly in boiling alcohol till the soluble part is taken up, neglecting the residue, which is a mild inert matter. This alcoholic solution is yellow and excessively acrid. Evaporate this nearly to dryness, then put the extract which is left, into a phial with cold sulphuric ether, and frequently shake them. In a day or two the ether becomes of a pale yellow. Pour off the clear ethereal solution and let it evaporate totally in the air. It will deposit scales resembling mica, mixed with a little oil which alcohol will remove. These scales are intensely acrid, and seem to contain nearly all the blistering properties of the fly itself. The smallest visible portion of them dissolved in oil when applied to the skin, will raise a blister in an hour or two.

The residue of the cantharides in substance, after the decoction in water is poured off, will give a tincture to alcohol, which when evaporated leaves a green unirritating oil.

**CARBON. CARBONIC ACID DIAMOND.**

We have to give a short account of two or three very important series of experiments on the combustion of different species of charcoal, on the proportions of base and oxygen in carbo-

nic acid, and on the supposed identity of the diamond with charcoal.

The first to be mentioned are those of Messrs. Allen and Pepys.<sup>b</sup>

The object of these accurate chemists was to consume certain known quantities of diamond and other carbonaceous substances in oxygen gas and thereby to determine the quantity of carbonic acid produced. The apparatus consisted of a platina tube, holding a platina tray that contained the substance to be burned, and was itself strongly heated by a furnace into which the tube was inserted. The tube was connected with and between two mercurial gasometers, and these were so contrived that oxygen gas could be transmitted alternately from one gasometer to the other, each time passing through the ignited platina tube that contained the substance to be examined.

The oxygen gas was prepared from oxymuriat of potash, and used a few hours after it had been procured; its purity being first ascertained by the eudiometrical test of sulphat of iron holding nitrous gas in solution, to absorb the oxygen of the portion analyzed, followed by simple sulphat of iron to absorb any nitrous gas that might have been expelled from the first liquid.

The charcoals which were made the subject of the first experiments were prepared directly from different kinds of wood, each of which was put into a small crucible and covered with sand, and was gradually ignited and finally kept for about 40 minutes at a white heat. In this way the woods employed yielded from 15 to 20 per cent. of their weight of dry charcoal. As it was found that dry charcoal when exposed to the air increased from 10 to about 20 per cent. of its weight by the absorption of moisture, the specimens employed for the experiments were again heated immediately before the experiment and weighed whilst still warm.

The gasses were all estimated at the same temperature of 60°, and at 30° inches barometer. The correction for expansion by heat was taken from the datum of Gay Lussac, who asserts, that air expands 0.00208, or  $\frac{1}{480}$  part of its bulk, for every degree of Fahrenheit from 32° to 212°, which very nearly agrees with Mr. Dalton's estimation. The quantity of gas to be estimated was therefore divided by 480, and the quotient multiplied by the degrees of difference from 60° for the correction for temperature.

A preliminary object was to estimate the exact weight of oxygen and carbonic acid gas.

<sup>a</sup> Ann. Chim. tom. 76.

<sup>b</sup> Phil. Trans. for 1807.



The carbonic acid gas was obtained from marble and dilute sulphuric acid, and was of such purity that 99 parts out of 100 were absorbed by lime water.

A glass globe previously exhausted of air, was filled with 21 cubic inches of the carbonic acid gas in the state in which it was procured, which weighed 10.2 grains at 44° therm. and 29.86 bar.

These 21. cubic inches equalled 21.58 at mean pressure and temperature, and hence 100. cubic inches of carbonic acid gas weigh under these circumstances 47.26 grains.

Oxygen gas was then obtained from oxymuriat of potash over mercury, which when analyzed by the nitrous sulphat of iron, left an unabsorbed residue of only 2 in 100. The glass globe holding 21 cubic inches was filled with this oxygen under the same pressure and temperature, which weighed 7.3 grains. Hence the weight of 100 cubic inches of oxygen of 98 per cent. purity weigh at 60° ther. and 30° bar. 33.82 grains.

The experimenters then ascertained by trials on known mixtures of carbonic acid gas and oxygen, that lime water would extract the whole of the carbonic acid from such a mixture.

The experiments on the combustion of charcoal were then performed by passing oxygen from one gasometer to the other through the platina tube containing the charcoal already heated to redness. The results of each experiment were as follows:

1. Four grains of Box-wood charcoal were all consumed except 0.02 grains of ash, and produced 13.76 grains of carbonic acid, which occupied exactly the same volume as the oxygen of which it was composed. No flash of light was observed during the combustion, whence the absence of hydrogen was inferred. The 3.98 grains of pure charcoal took 9.85 grains of oxygen for its combustion, which should therefore have produced 13.83 grains of carbonic acid. The actual quantity of carbonic acid obtained was 13.76 grains, making a difference of only .07. It may be observed that on analyzing the entire gas at the end of the experiment, after removing the carbonic acid gas by lime-water, and the oxygen by nitrous sulphat of iron, exactly the same proportion of unabsorbed residue was left as the oxygen itself furnished before the experiment, whence it was inferred by the experimenters (and with great probability) that no gas whatever was furnished by the combustion of the charcoal except car-

bonic acid. This residue however was not actually analyzed, but was taken as azote.

Calculating from the quantity of oxygen and charcoal actually consumed in this experiment, the carbonic acid should be 13.83 grains, which would give 28.77 grains of charcoal in 100 grains of carbonic acid.

Calculating from the volume of carbonic acid actually produced, which was 29.13 cubic inches, its weight (from the data originally found) must be 13.76 grains, which contained the 3.98 grains of charcoal consumed, and hence 100 grains of carbonic acid must contain 28.92 grains of charcoal.

2. The second experiment was on the combustion of transparent Brazilian diamond. This was performed precisely in the same manner as the last. The oxygen gas was repeatedly passed over the red-hot diamonds for ten minutes. The combustion did not raise the heat to whiteness as with charcoal, as it went on more slowly. The portions of diamond that remained unconsumed at the end of the experiment were all reduced to an opaque white substance resembling enamel. There was no discolouration of the platina vessel nor any ash whatever. Out of 3.95 grains of diamonds employed, 2.49 grains were consumed. The results will be given presently in a tabular form. No water whatever was condensed in the gasometer after the experiment.

3. A second experiment was made on 4.01 grains of diamonds. In a quarter of an hour they were totally consumed, and not a vestige left.

4. The next experiment was made on Welch stone-coal or culm, used by maltsters, which contains little or no maltha, and burns without flame. This was previously strongly heated under sand. The oxygen was passed over four grains of it in the platina tube for ten minutes, and the whole was consumed except half a grain of residue.

5. Plumbago was next tried. In a quarter of an hour 4 grains of it were consumed except .2 of a grain of oxyd of iron.

6. Muscular fibre distilled in a coated glass retort, left a black shining animal charcoal, 4 grains of which were put into the platina tube and heated. The first time the oxygen gas passed over it, a lambent flame filled the whole of the glass tube, connecting the platina tube with the gasometer. After the experiment, a minute portion of charcoal remained; and a quantity of saline matter adhered to it so firmly,

that it became impossible to ascertain the carbon consumed.

7. Some of the animal charcoal was heated to redness under sand for an hour, after which 4 grains of it were put into the platina tube. On first passing the oxygen over it, flashes ran along the glass tube, and the whole gas became cloudy. The platina tube after the experiment had lost 3.2 grains, but this loss was not wholly carbon, as some of the salts contained in the animal charcoal might have been volatilized by the heat, and in fact the inner surface of the gasometers was slightly covered with an efflorescence. To make this experiment agree with the former ones, it is necessary to suppose half a grain of volatile matter in the 3.2 grains of charcoal.

The results of the above experiments, excluding those on animal charcoal, gave the following weight of carbon in 100 carbonic acid.

	Estimating by Carbonic Acid.	—	Estimating by Oxygen.
Box-wood Charcoal	28.92	—	28.77
Diamond, 1st expt.	28.95	—	28.81
Diamond, 2d expt.	28.82	—	28.72
Stone Coal	28.20	—	28.27
Plumbago	28.46	—	28.46

The mean of the first column of numbers is 28.67, and of the second 28.60. The authors however mention with great candour, that two experiments with box-wood charcoal gave 29.75 and 30.68 per cent. of carbon; and one experiment with diamond gave 29.96, all of which are rejected from the mean estimate as being inaccurate.

The general inferences from these experiments are, that 100. grains of carbonic acid contain about 28.6 grains of carbon: that well burnt charcoal contains no sensible quantity of hydrogen, but if exposed to the air for a few minutes, it absorbs moisture, which renders the analysis in this state uncertain: and that charcoal cannot with any propriety be considered as oxyd of diamond, since it requires full as much oxygen to be converted into carbonic acid as diamond does.

We may add too that these experiments confirm the fact first observed by Lavoisier, that when oxygen gas is converted into carbonic acid by the combustion of charcoal, no change what-

ever takes place in the volume of the gas, so that in all analyses one measure of pure carbonic acid may be safely assumed as indicating the same measure of oxygen gas.

The above experiments are valuable for the accuracy with which they appear to have been performed, and the fidelity with which the results are related, but two defects have been pointed out. One of them is, that in no instance were any of the gasses stated to have been freed from hygrometric moisture, which defect is particularly to be noticed in the estimation of the carbonic acid gas, since in the experiment by which the weight of this gas was first ascertained, it was procured in the moist way directly from marble and sulphuric acid; but in the subsequent experiments the carbonic acid was formed by ignition of charcoal carefully dried.

The other defect is, that all the gas after combustion was analyzed only by lime-water to absorb the carbonic acid, and by nitrous gas in sulphat of iron to remove the oxygen; the residue unabsorbed by either being assumed as azote without further examination. However, as this unabsorbed residue in every instance almost exactly corresponded with the original azotic impurity of the oxygen employed, this omission is perhaps of less importance than the other.

The next series of experiments on this subject which we shall mention, are those of Theodore de Saussure,\* which were conducted with the express view of avoiding certain sources of error presumed in those just related.

The first object was to find the specific gravity of oxygen and carbonic acid. The author gives the weight of a cubic decimetre (61.028 E. cub. inch.) of oxygen gas not freed from hygrometric moisture to be 1.3552 grammes (20.88 Eng. grains) at 12.5° cent. therm. (54.5° Fahr.) and at 0.758 metre pressure (29.843 Eng. inches.)

The weight of the same quantity of moist carbonic acid gas under similar circumstances, is given at 1.8578 grammes (28.6918 Eng. grs.) When these are reduced to English weights and measures, it will be found as follows:

100 cubic inches of undried oxygen at 30° Bar. and 60° Therm.	weigh	34.003
100 ditto	of undried carbonic acid	46.727

These numbers, it may be remarked by the way, somewhat differ from those of Messrs. Allen and Pepys, who give 33.82 grains for the oxygen, and 47.26 for the carbonic acid.

M. Saussure performed the combustion of the carbonaceous substances in a tubulated receiver of about 5  $\frac{1}{2}$  pints capacity, and ignited them by a burning lens. The charcoal was suspended

\* Ann. Chim. tom. 71.

on a platina dish, and a small vessel full of dry muriat of lime previously weighed was placed in the tubulure of the vessel. The receiver was first filled with mercury, which was replaced by oxygen gas extracted from oxymuriat of potash, and another small glass vessel was adopted, in which a portion of the gas could be withdrawn for examination.

The analysis of the gas was performed in the following way. The oxygen was extracted by hydrosulphuret of potash saturated with azotic gas, which was allowed five days for its operation without agitation, and with care to preserve a nearly uniform temperature, that no portion of the azote contained in the eudiometric liquor should be expelled. This method he observes is more exact than Volta's, of detonating the oxygen with hydrogen, when the only impurity mixed with the oxygen is azotic gas; but Volta's is preferable where any carburetted hydrogen is present, as the sulphuretted liquor absorbs a sensible portion of this latter gas.

To separate the carbonic acid gas, the author prefers a small bulk of a very concentrated solution of caustic potash; for he finds by direct experiment that lime-water, or rather the water alone, absorbs a little oxygen by agitation as well as all the carbonic acid gas, when no great proportion of azote is present. Therefore though lime-water will accurately separate the carbonic acid alone from a mixture of this gas with common air, it cannot be depended on to give such exact results with a mixture of carbonic acid and oxygen. Messrs. Allen and Pepys had ascertained the accuracy of lime-water in the former case, but not in the latter.

The author further observes, that when any substance containing hydrogen, such as wood, oil, &c. is burnt in oxygen gas, a small quantity of the hydrogen escapes combustion, however great the excess of the oxygen is, and even cannot be ignited in this excess of oxygen by the electric spark. The only way of detecting and estimating this hydrogen, is to add 100 additional measures of hydrogen to 200 of the impure oxygen to be examined, which are then in the proportions capable of detonation; and then to observe whether the condensation is greater than would be produced by pure hydrogen and oxygen, allowing 200 measures of the former to condense 100 of the latter. M. Saussure asserts that every kind of hydrogen, even that obtained by the electrization of pure water, contains a small portion of carbon, so as to furnish a sensible quantity of carbonic acid when burnt with the purest oxygen which has pre-

viously been agitated with potash. This carbonic acid he finds to be about 3 measures from 1000 of hydrogen and 1000. of oxygen, but it is only made sensible when an excess of oxygen is employed; for when, on the contrary, an excess of hydrogen is used, scarcely any indications of carbonic acid are given, but the author asserts that then the unconsumed hydrogen is to a certain degree oxy-carburetted.

When a mixture of oxygen and azote is exposed to the electric spark with hydrogen in Volta's eudiometer, a sensible quantity of the azote is condensed, which in a single detonation may amount to 2 per cent. of the azote present. When much oxygen remains after the combustion, the condensed azote furnishes nitric or nitrous acid; but when the hydrogen is in excess, the azote produces nitrat of ammonia. This same ammoniacal salt is always generated by the slow combustion of hydrogen and of oxy-carburetted hydrogen in the open air.

The carbonaceous substances burnt in these experiments were plumbago, anthracite, charcoal arising from the decomposition of oil of rosemary, box-wood charcoal, and the charcoal which remains after passing the vapour of sulphur through it in the preparation of carburetted sulphur. The mode of performing these experiments was considerably complicated, as may be inferred from the preliminary eudiometrical remarks.

We shall select the experiment on the combustion of plumbago: 0.588 grammes of Cornish plumbago dried at a red-heat was burned in the receiver full of oxygen gas for an hour by the sun's rays collected through a lens. There remained 0.33 grammes of red oxyd of iron, the oxygen of which was .0099, and the iron therefore was .0231, and hence the carbon consumed was  $0.588 - 0.0231 = 0.5649$ . The gas before combustion, reduced to the standard pressure and temperature, was 1758.8 cubic centimetres, and after combustion 1750.4, giving a diminution of 8.4. The vessel of muriat of lime enclosed in the receiver had increased in weight 5 centigrammes, one of which is to be reckoned as the moisture absorbed from the air during the short time of its introduction into the vessel before the experiment, so that the moisture absorbed from the gas alone was 4 centigrammes, which is within  $\frac{1}{50}$  of the quantity of moisture contained in the undried oxygen at the temperature employed. Hence it appeared that no water was produced by the combustion of the plumbago.

The oxygen examined before combustion, by the test of hydrosulphuret of potash, shewed

10.25 measures in 200 of azotic impurity; 200. measures of the same oxygen were also detonated with 400. of hydrogen, and the whole was reduced to 33 measures, so that 567 measures had disappeared in the form of water. Of this, one third is the oxygen, amounting therefore to 189, and if to this be added the 10.25 of azote found by the hydrosulphuret, the whole 200 of the oxygen employed will be accounted for, except 0.75, which is too small to be noticed. Hence the gas before combustion, consisted of

1669.8	measures of oxygen
89.	azote

---

1758.8

The gas after combustion amounted to 1750.1. measures, from 100 of which the caustic potash absorbed 63.42 of carbonic acid. Another portion of the same gas was detonated with a mixture of equal parts oxygen and hydrogen, and the residue with potash to absorb the carbonic acid always produced by the combustion of oxygen and hydrogen, arising (as the author asserts) from the carbonic impurity of the hydrogen. The diminution of volume and the carbonic acid produced were no more than would arise from the hydrogen added to effect the detonation, whence it is inferred that no hydrogen was elicited by the combustion of the plumbago. Another 100 parts of the gas remaining after the experiment, examined by hydrosulphuret of potash, shewed 87 of oxygen and 13 of azote; and another 100 parts of the same gas detonated with 200 of hydrogen were reduced to 40. shewing 86.66 per cent. of oxygen and 13.34 of azote. Hence the composition of the 1750.4 measures of gas remaining after the combustion of the plumbago, is the following:

Cubic centimetres.	
1110.1	of carbonic acid gas
557.06	oxygen gas
83.24	azotic gas

---

1750.4

If the combustion of the carbonic acid is inferred from the quantity of oxygen gas required to produce it, it will be found that the volume of oxygen gas consumed by the combustion is, 1669.8—557.1=1112.7 cubic centimetres, of which 7.3 are employed to oxydate the iron, leaving 1110.1 as the oxygen entering into the carbonic acid produced. Hence converting the measures to their equivalent weights, and adding the weight of the plumbago consumed, the com-

position of 100. parts by weight of carbonic acid will be 72.64 oxygen and 27.36 carbon.

If the computation be made from the weight of the plumbago consumed, and that of the carbonic acid consumed, the proportions of 100. parts of this acid will be 72.61 oxygen, and 27.39 carbon.

The combustion of box-wood charcoal conducted in the same manner, gave 72.85 of oxygen to 27.15 of carbon.

The charcoal of essential oil shewed 72.88 oxygen to 27.12 carbon.

As no hydrogen appeared to be given out, either from the charcoal of essential oil, or from the plumbago, it would appear that these are the experiments on which the greatest confidence may be placed, and the mean of these gives for the composition of 100. parts by weight of dry carbonic acid, 27.29 parts of carbon and 72.71 of oxygen.

A second series of experiments on the combustion of diamond and other carbonaceous matter has been undertaken by M. Guyton Morveau.<sup>4</sup> The apparatus employed by this eminent chemist nearly resembled that of Messrs. Allen and Pepys, and consisted of two gasometers connected by a tube, the center part of which was of platina and was passed through a furnace. The substance to be burnt was enclosed in the platina tube, and oxygen gas was passed over it repeatedly from one gasometer to the other as long as the experiment lasted.

M. Guyton made the very important addition of a tube filled with dry muriat of lime enclosed in each gasometer to absorb any moisture, and the gas immediately on entering and quitting the platina tube, was exposed to artificial cold to enable it more completely to part with any moisture which it might contain. As the oxygen was previously dried, any moisture condensed in the tubes of muriat of lime was inferred to arise from the generation of water by the hydrogen of the substance burned, with the oxygen employed. Hence this hydrogen was estimated at  $\frac{1}{100} \frac{1}{100} \frac{1}{100} \frac{1}{100}$  of the increase of weight acquired by the muriat of lime.

M. Guyton estimates the weights of all the gasses concerned to be as follows: the pressure being 0.758 metre, (29.8432 Eng. inches) and 12.5° cent. Ther. (54.5° Fahr.)

One litre of	weights	Grammes.
Dry Oxygen gas	—	1.3435
— Common air	—	1.2247
— Azotic gas	—	1.1987
— Hydrogen gas	—	0.1032
— Carbonic acid gas	—	1.8372

<sup>4</sup> An. Chim. tom. 84.

The composition of water is assumed to be (by weight.)

Oxygen	—	85662
Hydrogen	—	14338
		—————
		100000

And of carbonic acid (by weight)

Oxygen	—	72624
Carbon	—	27376
		—————
		100000

And of carbonat of barytes (by weight)

Carbonic acid	—	221.
Barytes	—	779.
		—————
		1000.

The weight of the litre of dry carbonic acid reduced to English measure is as follows: 1 litre = 61.028 Eng. cub. inches, and 61.028 cub. in. at 29.8432 inch pressure = 60.709 cub. in. at 30 inches. And 60.709 at 54.5° therm. Fahr. = 61.404 cub. in. at 60° Fahr. allowing the expansion of  $\frac{1}{480}$  for every degree of this thermometer. And 1.8373 grammes (the weight of a litre of dry carbonic acid) equals 28.3737 troy grains, and hence 100. cub. inches of dry carbonic acid at 30. inches bar. and 60°. therm. weigh 46.20 Troy grains.

M. Guyton's experiments gave the following results. The combustion of 1.435 grammes of oak charcoal, previously heated by itself, caused the deposition of only 0.065 grammes of water, the hydrogen of which is 0.00932, which therefore does not exceed  $\frac{1}{10000}$  of the charcoal burnt.

Cumberland plumbago in the same way was inferred to contain  $\frac{1}{10000}$  of hydrogen.

Piedmont plumbago contained  $\frac{1}{10000}$  of hydrogen. Diamond in one experiment shewed  $\frac{1}{10000}$  of hydrogen; but another more accurate trial gave at the utmost not more than  $\frac{1}{10000}$ , and part of this small quantity might possibly be furnished by the water of crystallization which may be supposed to exist in this crystallized form of carbon.

From the general results of these experiments it does not appear that any decided chemical difference can be detected between diamond, pure plumbago, and charcoal.

CARBURETTED HYDROGEN. OLEFIANT GAS. CARBONIC OXYD. OXYCARBURETTED HYDROGEN. COAL GAS.

<sup>a</sup> Mem. d'Arcueil, tom. 2.

The constitution of the compound inflammable gasses, obtained by the distillation of vegetable matter or of moist charcoal, is a subject of extreme difficulty, which has given rise to various opinions among chemists. The only substances that constantly compose these gasses are carbon, hydrogen, and oxygen, but the respective proportions of these vary greatly, and the only mode of certain analysis is by compleat combustion with oxygen, thus reducing the whole to carbonic acid and water. It is obvious therefore that this mode of examination will not resolve the question of the intermediate composition of these gasses, but will only give their ultimate analysis, so that a gas may consist, for example, either of a triple compound of oxygen, carbon and hydrogen, (oxycarburetted hydrogen) or may be a compound of carburetted hydrogen and carbonic acid, and in each case will afford precisely the same results by ultimate analysis into carbonic acid and water.

Berthollet has asserted that all these gasses produced either by the distillation of moist charcoal or by the destruction of vegetable matter at a high heat contain oxygen, and are properly species of oxycarburetted hydrogen, the elements of which may combine in infinite proportions. He finds this opinion, partly on his own experiments on the products of moistened charcoal, and partly on those of Th. de Saussure on the gasses produced by passing the vapour of ether and alcohol through an ignited tube; all of which are found to contain a notable quantity of oxygen. On the other hand, it is maintained by Dalton, Thomson, Henry, and other eminent chemists, that there are two distinct species of carburetted hydrogen, namely, the pure *Carburetted Hydrogen*, a natural product of stagnant waters in the summer; and that singular gas obtained by the distillation of sulphuric acid and alcohol, called by the inventors *Olefiant Gas*, or, from its composition, it may be termed *Super-carburetted Hydrogen*. A mixture of these two species with pure hydrogen and with carbonic oxyd, and with empyreumatic oil, will (according to these chemists) account for all the known varieties of specific gravity and of oxygenation in all the other compound gasses. We shall merely give a short abstract of some of the most important experiments.

Those of Dr. Thomson are highly interesting.<sup>b</sup> He considers the great variation in the specific gravity of the gasses obtained by dis-

<sup>b</sup> Phil. Journ. vol. 88. p. 321.

tilling coal and other oily substances as chiefly owing to the oil held in solution by the gas. He therefore selected for analysis the gas that rises in considerable quantity from stagnant waters during the summer season, which had been before examined by Cruikshank and Dalton. This gas always contained 12.5 per cent. of common air, and from 5 to 7 of carbonic acid, which latter being removed, the specific gravity of the remaining gas was 0.611, equal to 0.554 after the removal of the common air, the specific gravity of the latter being 1.000. This gas burns with a large yellow flame, and detonates when mixed with not less than its own bulk of oxygen and ignited. On an average 100 measures of this gas ignited with 205. measures of pure oxygen form 104 of carbonic acid gas. But as carbonic acid contains only its own bulk of oxygen, the 104 parts only employed 104 of the 205 of oxygen consumed, and hence the 101 remaining measures went to the production of water and required 202 measures of hydrogen for that purpose. Reducing these to the proportions by weight (reckoning carbonic acid to contain 27.5 per cent. of carbon) the composition of the pure carburetted hydrogen of this gas from stagnant water would give nearly as follows:

Carbon . . .	72.
Hydrogen . . .	28.
	100.

In fact the sum of the constituent parts thus found would rather exceed the weight of the original gas, which at any rate would shew that no oxygen nor any other ponderable substance could be present. If this analysis is correct, and it agrees very nearly with that of Dalton, this gas (after extracting the common air and carbonic acid) is not an oxycarburetted hydrogen but a simple carburetted hydrogen, and is considered by Mr. Dalton as composed of one atom of carbon and two atoms of hydrogen.

Olefiant gas is the next definite compound examined by Dr. T. It was obtained in the usual manner by mixing one measure of alcohol with three of sulphuric acid, and boiling the mixture almost to dryness in a small retort, and collecting the gaseous product over water. This consisted of olefiant gas mixed with carbonic acid, which last increased in proportion as the process was continued.

This olefiant gas deprived of carbonic acid but retaining 16 per cent. of common air, was

found to have the specific gravity of 0.9786, hence, by calculation, pure olefiant gas would give 0.9745 sp. gr. (common air being 1.000.)

Olefiant gas when mixed with thrice its bulk of oxygen and ignited, detonates with extreme violence and produces twice its bulk of carbonic acid, according to Mr. Dalton, which very nearly coincides with Dr. Thomson's experiments. A hundred cubic inches of it (at 60° therm. and 30. bar.) weighed 29.72 grains. The weight of its constituent parts (considered merely as carbon and hydrogen) as found by analysis, somewhat exceeded the gas employed, a proof that it could contain no oxygen.

In average numbers it may be considered as containing

Carbon . . .	85.
Hydrogen . . .	15.
	100.

Mr. Dalton considers it as containing an atom of carbon and an atom of hydrogen.

Olefiant gas derives its name from its forming a singular oily-looking liquid when mixed with oxymuriatic gas, as already described (Chem. Dict. vol. I. p. 257.) Dr. Thomson has further examined this curious substance. A large bottle was filled with olefiant gas and a current of oxymuriatic gas being passed into it, the oily substance soon collected at the bottom. Its colour was greenish-white. When dropped into water it fell to the bottom, but gradually dissolved in it by agitation, and gave the water a sweet and cooling taste, and a slight aromatic odour. It dissolved completely in alcohol and sulphuric ether, but not in oil of turpentine. When left in an open vessel it evaporated, leaving only a greenish trace. It appears therefore to be totally distinct from the oils.

Olefiant gas is also obtained as a small part of the compound inflammable gas from coal, from caoutchouc, from mineral tar and other combustible bodies. It is separable from common carburetted hydrogen by oxymuriatic gas as will be further noticed.

Olefiant gas has been more lately analyzed by Th. de Saussure.\* To diminish the extreme violence of the detonation where this gas is ignited with about thrice its volume of oxygen (the quantity that saturates it) the author employed a much larger proportion of oxygen. The general results were the following: 100. parts, in volume, of olefiant gas, were detonated

\* An. Chim. tom. 78.

with 500. of oxygen deprived of carbonic acid, but containing 23.5 of azote. The mixed gasses were reduced by the detonation to 409.5 parts, from which potash extracted 201. of carbonic acid, and hydrosulphuret of potash 184.5 of oxygen, leaving 24 parts of azote. Hardly  $\frac{1}{100}$  of the olefiant gas escaped combustion, for, on adding a known quantity of hydrogen to part of the entire residue of the detonation and again exploding it, the diminution was scarcely more than would have been produced by adding the hydrogen alone, and sufficient oxygen.

By subtracting the oxygen of the carbonic acid produced in this experiment from the entire quantity consumed, and finding the weight of hydrogen required to convert this remaining oxygen into water, the author finds in 100 parts, by weight, of olefiant gas, 84.78 of carbon and 13.55 of hydrogen, reckoning 27.2 of carbon in 100. of carbonic acid. This computation leaves only 1.67 of the 100. parts of olefiant gas unaccounted for, which is quite within the limits of unavoidable errors; for, in another experiment conducted in the same way, the sum of the carbon and hydrogen a little exceeded the olefiant gas employed. Hence M. de Saussure concludes that pure olefiant gas, in the preparation of which the distillation has not been carried too far, contains no oxygen, but is composed simply of about 86. of carbon and 14. of hydrogen, proportions which agree very closely with those of Dalton and Thomson. The specific gravity of this gas was about .985, common air being 1.000. If 15 parts by weight of hydrogen condense to half their volume by dissolving 85 parts of carbon, the resulting olefiant gas would by calculation, be found to have nearly the above specific gravity.

It has been mentioned in the original article (Ch. Dict. vol. 1, p. 257) that when olefiant gas is exploded with little more than its own

bulk of oxygen, so much carbon is precipitated in substance as entirely to blacken the vessel. Dr. Thomson has repeated this experiment, employing rather less oxygen than olefiant gas. After the explosion, the bulk of the residue is much greater than that of the gasses before explosion, being increased in about the proportion of 16 to 10.; or in still greater proportion if the uncombined oxygen that remains in the residue be removed. This residuary gas is much lighter than olefiant gas, having the specific gravity of only 0.48, and is considered by Dr. Thomson as a proper *oxy-carburetted hydrogen*, or triple compound of oxygen, carbon, and hydrogen, and the proportions would nearly indicate the combination of an atom of each of these elements.

A great number of interesting experiments have been made at different times by Dr. Henry, on all the above described inflammable gasses, more particularly with a view to direct the economical use of the gas procured from the distillation of coal, which has now become an object of considerable national importance. Dr. Henry's first series of experiments, though confessedly imperfect, requires a short notice in this place.<sup>d</sup> Dr. Henry constructed an Argand lamp, to be supplied with gas instead of oil, and found that both pure hydrogen and carburetted hydrogen, from moist charcoal, and carbonic oxyd, gave so trifling a light as to be entirely unfit for the purposes of illumination; while on the other hand the gas distilled from coal, gave a light little inferior to that from good spermacetil oil. Neither is this difference materially owing to any oily matter mechanically suspended in the coal gas, since it retains its power of burning with a bright dense light after being long kept over water, though somewhat impaired in intensity. The following gasses were then burnt with oxygen in close vessels, and the comparative quantities required for saturation were noted.

Kind of Gas.	Oxygen required to saturate 100 measures.	Carbonic Acid produced!
Pure Hydrogen	50	0.
Gas from moist Charcoal	60	35.
— Wood	54	33.
— dried Peat	68	43.
— Cannel Coal	170	100.
— Lamp Oil	190	124.
— Wax	220	137.
Pure Olefiant Gas	284	179.

<sup>d</sup> Phil. Journ. vol. xi. p. 65.

As there is much variation in the quality of most of these gasses, according to the circumstances in which they are procured, the above numbers are not to be considered as universally applicable, but they shew in a very satisfactory manner the comparative combustibility of this substance, as measured by the quantity of oxygen required for its consumption, and thus will account for the much greater intensity of light given by the latter over the former gasses. Above all others, the olefiant gas is as much distinguished by the splendour and beauty of its light as it is by the very superior quantity of oxygen which it requires for its combustion.

The specific gravity also of the gas is in some degree a test of the quantity of combustible matter which it contains, being in greater quantity as the gas is heavier, though this does not apply to carbonic oxyd but only to carburetted hydrogen.

In a later paper, Dr. Henry describes an apparatus of his own construction, for the better analysis of these gasses, which enables him to employ much larger quantities, and to consume them by slow continued combustion, which he considers as a much more accurate mode of analysis than by sudden ignition with oxygen in Vol. a's eudiometer.\* But most of the gasses obtained by distillation of any combustible, and especially that from coal, which is the most important in the present view of the subject, are mixtures of several gasses, and cannot be properly analyzed by mere combustion with an excess of oxygen. Coal gas when first obtained consists of, carbonic acid, sulphuretted hydrogen, olefiant gas, and the remainder, which is by far the greater portion, is either a gas *sui generis*, an *Oxycarburetted Hydrogen*, or else a mixture of carburetted hydrogen and carbonic oxyd. It is therefore an important problem in analytical chemistry to be able to estimate these separately. Dr. Henry gives the following way, as at least affording an approach to accuracy in obtaining this object.

Sulphuretted hydrogen is absorbed by liquid potash, and by oxymuriatic gas.

Carbonic acid is absorbed by liquid potash, but is not altered by oxymuriatic gas.

Olefiant gas is immediately decomposed or absorbed by oxymuriatic gas, and is speedily absorbed by water, but is not acted on by liquid potash.

Carburetted hydrogen is not altered by oxymuriatic gas, except after some hours' contact, and it is not sensibly changed by water.

Therefore to analyze a coal gas (for example) first add two measures of the recent coal gas to one measure of oxymuriatic gas, and after a minute or two observe the diminution. Then wash an equal quantity of the coal gas with liquid potash to extract the sulphuretted hydrogen, and submit the residue to oxymuriatic gas as before. The second diminution by oxymuriatic gas, divided by 2.2 gives the proportion of olefiant gas. Deduct this absorption from the first, and divide the remainder by 1.8 for the quantity of sulphuretted hydrogen. Lastly, to find the quantity of carbonic acid, subtract from the entire diminution by potash the amount of the sulphuretted hydrogen.

By these operations the amount of the carbonic acid, sulphuretted hydrogen, and olefiant gas will be found, and when these are separated, there will remain only the oxycarburetted hydrogen, or mixture of carbonic oxyd and carburetted hydrogen (whichever it may be) which can only be analyzed by complete combustion with oxygen to determine separately the oxygen, carbon, and hydrogen, but which will not show the mode of constitution of the gas, but only the actual constituent parts.

The following general remarks on these gasses may be added. The olefiant gas is a very sparing product of the distillation of pit-coal. It is found only in the first portions, and does not compose more than 5 per cent. of these. It is absorbed in no great length of time by being in contact with water, and hence much washing of the gas or keeping it long over water is detrimental to its quality, since the olefiant gas is eminently combustible, and gives more light than any known species of inflammable gas containing either carbon or hydrogen. The gas from mineral tar or from caoutchouc, contains about one-tenth of olefiant gas.

Sulphuretted hydrogen is most abundantly produced from coal in the earlier stage of distillation, and then constitutes from one to five per cent. It increases the light of the gas but is unpleasant and injurious, by the sulphurous acid gas which its combustion generates. Part of the sulphuretted hydrogen unites, in the act of formation, with the ammonia of the coal, forming sulphuret of ammonia, which may be detected in the condensed products. Carbonic acid gas also appears only in the first products, and only in small quantity, never amounting to 5 per cent. The entire gas from coal undergoes a gradual diminution of combustibility, and with it, of specific gravity, during the

\* Phil. Trans. for 1808.



whole distillation. Some of the latter products are so light that they can hardly be explained without supposing an evolution of pure hydrogen along with the other gasses. A cubic foot of coal-gas of medium quality, viz. of .622 specific gravity, such as is first afforded by the distillation of Newcastle coal, is stated by Dr. Henry to weigh 333.5 grains. This will yield by combustion 817.3 grains of carbonic acid, of which the carbon (at 28.6 per cent.) will be 233.7 grains, leaving 99.8 grains for the hydrogen in the cubic foot of the same coal gas. This gas will therefore require 1128.5 grains of oxygen for its complete combustion, of which 573.6 grains will go to form the carbonic acid with the carbon, and the remaining 554.9 grains will form water with the hydrogen.

*Application of Coal Gas for the purpose of giving Light.* This important application of coal gas was first made in 1792, by Mr. Murdoch, then Engineer-agent at Redruth, in Cornwall, to Messrs. Boulton and Watts, of Birmingham, who carried on many experiments on the gasses distilled from different kinds of coal, peat, wood, and other substances, as a substitute for oil or tallow, in giving light.

In 1798 the coal gas was first actually employed by Mr. Murdoch, for the common purposes of illumination, at the manufactory of Messrs. Boulton & Watts, at Soho, and since that time its use has been extended to all the principal shops in this vast concern, to the exclusion of all other artificial light. Mr. Murdoch has given the following account of the gas-light apparatus employed in the extensive cotton mill of Messrs. Phillips & Lee, at Manchester, with all the adjacent store-rooms and counting-houses.<sup>§</sup> The total quantity of light used during the hours of burning, has been ascertained by a comparison of shadows, to be about equal to the light of 2500 mould candles, of six in the pound, each of the candles consuming at the rate of  $\frac{1}{4}$ ths of an ounce of tallow per hour. The coal is distilled in large iron retorts, which during the winter season are kept constantly at work, except during the intervals of charging, and the gas as it rises from them is conveyed by iron pipes into large reservoirs or gazometers, where it is washed and purified, previous to its being conveyed through other pipes, called *mains* to the mill. These mains branch off into a variety of ramifications, forming a total length of several miles, and terminate by burners, where the gas is con-

sumed, each of which is furnished by a cock to regulate the admission of gas, or to shut it off totally when not wanted. The burners are of two kinds, one resembles the common Argand lamp, the other is a small curved tube with a conical end, having three perforations of about a thirtieth of an inch in diameter, forming, when lighted, three divergent jets of flame. When the whole of the burners are used, the light is about equal (as already mentioned) to that of 2500 candles, and they require an hourly supply of 1250 cubic feet of the coal gas. The coal employed is the best Wigan cannel coal, which gives a gas much superior in quantity and quality to that of any other kind of coal. To supply two hours consumption of gas (which is about the daily average taking the year through) 2500 cubic feet of gas are required, to produce which, seven hundred weight of cannel coal must be distilled daily, or about 110 tons yearly.

About one-third of the above quantity of good common coal is required for fuel to heat the retorts. The 110 tons of cannel produce about 70 tons of good coak. Each ton of cannel coal gives from 11 to 12 ale gallons of coal tar. Mr. Murdoch adds the estimates of the expence attending each mode of illumination, by which it appears that where only two hours of daily average lighting are required, the annual expence of the coal gas is about £600, and that of an equivalent number of candles, is about £2000. A greater proportional saving is of course made by working the coal gas apparatus to its full extent, which in the present instance might be about equal to three hours daily consumption with the same apparatus.

The coal gas gives a peculiar soft, clear, and steady light, and it has the additional advantage over candles in requiring no snuffing and trimming, and therefore in avoiding one source of danger from fire, to which cotton mills are peculiarly exposed.

A very accurate description of a gas-light apparatus on the large scale, is given by Mr. T. Clegg,<sup>†</sup> with an illustrative plate. Mr. Clegg has actually put it in practice in several instances, and has succeeded in rendering the combustion of these lights free from any offensive smell. Indeed this smell chiefly, if not entirely, arises from the escape of a portion of the gas unconsumed. He estimates the cost of a complete apparatus capable of supporting forty lamps for four hours, each lamp afford-

<sup>§</sup> Ph. Trans. for 1805. p. 124.

<sup>†</sup> Ph. Journ. vol. xxiii. page 86.

ing light equal to ten candles of eight in the pound, to be about £250. Each lamp consumes six cubic feet of gas per hour.

Mr. B. Cook of Birmingham, has given the results of his experience in the employment of coal-gas light.<sup>a</sup> Among other advantages it is particularly convenient for that kind of soldering which is now performed with the oil-lamp, for the gas light gives a sharper flame, and is also ready at the instant, whilst with oil and cotton the workman is always forced to wait for his lamp being sufficiently kindled to do his work. Mr. Cook has also turned to great advantage the mineral tar which distills from the coal whilst the gas is preparing. Four pounds of the coarse tar are obtained, on the average, from every hundred weight of good coal; and this tar, when redistilled, will yield half its quantity of a volatile oil, fully equal to oil of turpentine for the purpose of japaning, and a residue will be left, nearly, if not quite, equal for the same uses to the best asphaltum. These varnishes obtained the honorary medal from the Society of Arts. Mr. Cook adds a minute account of the whole apparatus and processes for obtaining the gas and the spirit.<sup>b</sup>

**CARBURETTED SULPHUR.** See **SULPHUR Alcohol of.**

**CHABASIE.** Cubic Zeolite, J. Wurfel Zeolith, W.

Its colour is whitish, and sometimes pale-red superficially. It occurs crystallized in rhomboids, the obtuse angle of which is  $93\frac{1}{2}^{\circ}$ , either perfect or with the obtuse lateral edges truncated and combined with other modifications. It presents natural joints in three directions. It varies from transparent to translucent. Scratches glass with difficulty. Sp. gr. 2.7. Is readily fusible into a spungy white enamel; and is composed, according to Vauquelin, of

43.23	Silex
22.66	Alumine
3.34	Lime
9.34	Soda mixed with potash
21.	Water
<hr/>	
99.67	
0.33	loss

Chabasie occurs forming glands in trap rocks in the island of Ferroe, and lining the inside of agate geodes at Oberstein in the Palatinate.

**CHLORINE.** See **MURIATIC ACID.**

**CHLORINE AND AZOTE.** (*New deto-*

*nating compound of.*) See **AZOTIZED OXYMURIATIC ACID.**

**CHROME.**

In consequence of the abundant discovery of chromate of iron in France, M. Vauquelin has been induced to repeat his experiments on this substance, of which the following is a summary.<sup>a</sup>

*Decomposition of the native Chromate of Iron.*

This is best effected by levigating the ore, mixing it accurately with half its weight of nitre, and keeping it in a state of ignition for half an hour or more. The mass does not enter into fusion, yet the nitre is entirely decomposed and the alkaline base is generally completely saturated by the chromic acid. The mass is to be pulverized and very accurately lixiviated in water till every thing soluble is taken up. The residue is then to be digested with warm and dilute muriatic acid, which takes up the iron, the magnesia, the alumine and the silex. When the action of the acid has ceased, it is to be poured off whilst warm lest it should become gelatinous and thus impede its separation from the insoluble part. The residue not taken up by the acid, after being well washed is again to be mixed with nitre in the proportion of one-fourth of its weight and to be treated as at first. When thus by the alternate application of nitre and muriatic acid the entire decomposition of the chromate of iron has been effected, the alkaline solutions are to be added together, and after being saturated with nitric acid are to be crystallized. By this means a little earth and chromate of iron are got rid of; and thus, if all the processes have been performed accurately and if the nitre employed has been perfectly pure, there will be obtained pure chromate of potash.

*Oxide of Chrome.*

To a solution of chromate of potash add subnitrate of mercury, as nearly neutral as possible, as long as any precipitate takes place; this precipitate is chromate of mercury of an orange colour, verging more or less to yellow or red according to circumstances, and is to be repeatedly and very accurately washed in water in order to separate the whole of the nitre; being then strongly heated in a well luted earthenware retort till no more oxygen or mercury comes over, there will be obtained pure oxide of chrome the usual colour of which is green, but if the heat has been intense and long continued, it will be more or less of a brownish yellow.

<sup>a</sup> Ph. Journ. vol. xxi. p. 298.

<sup>b</sup> Ibid. vol. xxxi. p. 532.

<sup>c</sup> Ann. de Chim. lxx. p. 70.

If the mercurial solution employed in the foregoing process is at the minimum of oxydation and as nearly neutral as possible, the only substances remaining in solution in the mother liquor are nitre and nitrate of mercury, when an excess of this latter has been made use of. Generally however the mercurial solution contains a considerable excess of acid as well as a mixture of nitrate at the maximum of oxydation; and in this case the residual liquor exhibits an amethyst colour, and affords with alkalis a pale green precipitate, which after being heated is converted into oxide of chrome.

If this precipitate instead of being heated is digested with cold caustic alkali, it communicates to the liquor a bright green colour, and there remains undissolved a red powder exhibiting all the properties of the per-oxide of mercury. The alkaline solution itself when filtered and boiled, deposits a large quantity of flocculent green oxide of chrome, and acquires a golden yellow colour, being in fact an alkaline chromate of potash.

#### *Chromate of Barytes.*

This salt is most conveniently prepared by adding to a solution of pure and neutral chromate of potash nitrate of barytes as long as any precipitation takes place. The precipitate is insoluble even in a large quantity of warm water, and should therefore be washed repeatedly in order to free it entirely from any mixture of nitre.

Five grammes of this salt being dissolved in warm and dilute nitric acid, afforded on the addition of sulphuric acid in excess 4.4 grammes of sulphate of barytes: hence (estimating sulphate of barytes to contain 68 per cent. of base) chromate of barytes is composed of

62.6 Barytes
37.4 Chromic acid

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100.0

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Further, since 5 grammes of chromate of barytes contain 1.87 grammes of concrete acid, and since this latter by a strong calcination is reduced to 1.56 grammes of green oxide, it follows that 100 parts of green oxide require 16.6 of oxygen for their conversion into chromic acid.

#### *Chromic Acid and Oxide.*

The most convenient way of preparing chromic acid is to dissolve chromate of barytes in dilute nitric acid and then to precipitate the barytes by the addition of sulphuric acid, taking particular care not to leave this latter in excess.

The liquor is then to be filtered, and contains only nitric and chromic acids: in order to get rid of the first the whole must be evaporated to dryness repeatedly, with the precaution of not pushing the heat too much towards the latter end of each evaporation. When the chromic acid is much concentrated, it appears in the form of mammillated masses with intermixed crystalline grains: by exposure to the air it deliquesces. The colour of chromic acid is deep red, to the taste it is very acid and at the same time acerb and metallic: it is soluble in alcohol, but the solution soon becomes green owing to the partial decomposition of the acid.

If to a solution of chromic acid there be added a considerable quantity of sulphurous acid, the colour of the mixture becomes a dirty brown, from which caustic alkali throws down a reddish brown precipitate, soluble in acids. A still larger quantity of sulphurous acid changes the colour of chromic acid to a pale green; hence there appear to be two oxides of chrome, differing however but little in their respective proportions of oxygen.

The oxide of chrome procured by calcination of chromate of mercury, is very difficultly acted on by acids, but when recently precipitated it is soluble with ease, even in the weakest acids.

Muriate of chrome when evaporated to dryness, affords a rose coloured powder, which deliquesces in the air, and acquires a bright green colour. When calcined at a pretty considerable heat, it gives out an odour of oxymuriatic acid, increases in bulk, and is converted into micaceous scales of a brilliant yellow; by a further continuance of the heat, it passes into green oxide.

Caustic potash added in excess to any of the solutions of oxide of chrome in an acid, effects a solution of the oxide; the same takes place if recently precipitated oxide is digested in the same menstruum. The solution is of a deep green colour, but by ebullition the oxide is separated, and the liquor remains colourless.

#### *Alkaline, earthy and metallic chromates.*

There are two chromates of potash, the neutral and the acidulous. The former is of a lemon yellow colour, and crystallizes in minute prisms. The latter is of an orange red colour, and crystallizes in large prisms.

Chromic acid, when saturated by ammonia, and exposed to spontaneous evaporation, produces a salt of a bright yellow colour, which climbs up the side of the vessel; by boiling, it deposits a brown flocculent oxide, which acquires a green colour by calcination.

Chromate of lime is readily soluble in water, and affords by evaporation, silky scales, of a yellowish brown colour.

Chromate of magnesia is also readily soluble in water, and crystallizes in six-sided prisms, of a high topaz yellow.

Chromate of iron is formed by combining chromic acid, and the red oxide of the metal. But if a lower oxide is employed, (as in mixing green sulphate of iron and chromate of potash) a fawn coloured precipitate is obtained, which, when treated with caustic alkali, gives no trace of chromic acid: it is readily soluble in muriatic acid, and is precipitated without alteration from its solution by an alkali. Nitric acid effects a partial solution of it, and becomes of a green colour. Hence this compound is not chromate of iron, but a combination of chromic oxide and red oxide of iron, being perfectly analogous to the so called native chromate of iron.

Chromate of lead acquires different tinges of colour, according to the mode in which it is prepared; if the chromate of potash is perfectly neutral, the precipitate is of an orange yellow; if with an excess of acid, it is a full lemon colour; if on the other hand the alkali is in excess, the precipitate is full orange or scarlet. The acidulous chromate with nitrate of lead furnishes the most permanent colour.

Chromate of copper is most readily prepared by adding neutral chromate of potash to sulphate of copper; a yellowish brown precipitate falls down, which when well washed and dried, acquires a bistre colour.

Chromate of silver is best prepared by decomposing nitrate of silver by neutral chromate of potash; if the solutions before mixture are hot, the result is a brownish red precipitate, but a purple red precipitate if they are cold. If acidulous chromate of potash is employed, the precipitation takes place more slowly, is less abundant, and assumes the form of minute semitransparent crystalline grains of a carmine red. All the varieties of this salt become brown by exposure to the air. It is soluble in nitric acid, and decomposable with abstraction of the oxyd of silver by muriatic acid.

Oxide of chrome supports better than any other colorific substance, the intense heat required for baking the hard porcelain, and gives a perfect emerald green of great beauty and value.

#### CINNAMON STONE. Kancelstein, W.

Its colour is yellowish brown, passing into orange yellow and hyacinth red. It occurs in rolled and splintery fragments. Its internal

lustre is shining between vitreous and resinous; its fracture is imperfectly and small conchoidal, with joints not very visible parallel to the sides of a rhomboidal prism, the obtuse angle of which is about 100°. It is more or less transparent, scratches quartz, though with some difficulty, sp. gr. 3.6.

It is fusible before the blowpipe into a brownish black enamel. It has been analyzed by Klaproth, with the following result.

38.8	Silex
21.2	Alumine
31.25	Lime
6.5	Oxyd of Iron
<hr/>	
97.75	
2.25	Loss
<hr/>	

This mineral has hitherto only been found among sand, near Columbo, in the island of Ceylon. It was at first supposed to be a variety of zircon; but this, its chemical analysis amply disproves. By M. Mohs, it is regarded as possessing a marked analogy with garnet.

COAL GASS. See CARBURETTED HYDROGEN.

#### COBALT.

##### § 1. Ores of

##### *Native sulphuret of cobalt.*<sup>a</sup>

The colour of this mineral is pale steel grey. It occurs massive and botryoidal, in the latter case often presenting superficially the rudiments of crystals. Its fracture is uneven, passing into granular, and presents a metallic lustre.

On exposure to the blowpipe, it exhales a sulphureous odour unmixed with that of arsenic, it acquires a deep grey colour, and fuses into a brilliant fragil globule. If previously calcined and then mixed with borax, it affords a deep blue glass, and a white regulus, attractable by the magnet.

It has been analyzed by Hisinger, and appears to consist of

43.2	Cobalt
14.4	Copper
3.53	Iron
38.5	Sulphur
0.33	Earthy matter
<hr/>	
99.96	

It is a rare mineral, having been hitherto found only near Riddarhyttan, in Sweden, mixed with iron and copper pyrites.

##### § 2. *Chemical properties of Cobalt.*

Several useful observations on the salts and

<sup>a</sup> An. de Chim. lxxxiii. p. 329.

oxyds of cobalt have been made by Proust,<sup>b</sup> some of which we shall briefly notice.

*Oxyds of Cobalt.* The author reckons two oxyds, the grey and the black, the former of which is the *Suboxyd*, and the latter the *Peroxyd*.

The carbonat of cobalt is made by saturating the sulphat of this metal by carbonated potash. Of this carbonat, 100 parts heated gradually in a retort, filled as full as possible, till all the water and carbonic acid are expelled, give 60 to 62 of the grey suboxyd. This dissolves in nitric acid without giving out nitrous gas. When heated in contact with air, it absorbs oxygen, and passes more or less compleatly to the state of black oxyd. When the two oxyds are mixed, a weak acid will dissolve out only the grey oxyd, and leave the other. Pure ammonia does the same.

When a solid crystal of sulphat or nitrat of cobalt is thrown into a phial containing a weak solution of liquid potash, a violet blue precipitate is formed, which is the *Hydrat of Cobalt*, or more properly the *Hydrated Suboxyd*. When this is heated it loses about 20 per cent. of its weight, and becomes very pure suboxyd.

The hydrat is very soluble in acids without effervescence. When long kept under water it gradually absorbs oxygen, and becomes black oxyd. 100 parts of pure suboxyd reduced carefully in a close crucible, left 83½ of metal. Hence the author infers, that 100 parts of cobalt absorb 19 of oxygen to become grey oxyd.

The peroxyd is formed by distilling a nitrous solution of cobalt to dryness. Much nitrous gas escapes, and a black oxyd gradually separates. This peroxyd is insoluble without decomposition, in most acids; for when it does dissolve in them, it parts with oxygen in one form or other. It is also insoluble in ammonia. The cobaltic colouring matter of the beautiful blue glasses is the grey, and not the black oxyd. On the other hand, the carbonat and hydrat of cobalt become black oxyd by the contact of oxymuriatic acid. The nitrous and sulphurous acids dissolve the black oxyd without evolving oxygen, but the resulting salts are the nitrat and sulphat of cobalt.

The author estimates 100. of pure metal to absorb 25 or 26 of oxygen in becoming black oxyd.

*Muriat of Cobalt* is formed by dissolving grey oxyd in muriatic acid. The crystals of this salt are blue when quite *anhydrous*, but

become red in absorbing moisture. The green colour usually shewn by this solution, when used as a sympathetic ink, arises from the presence of a little nickel. When the black oxyd is heated with muriatic acid, oxymuriatic gas is given off, and the solution becomes the muriated suboxyd. This suboxyd also appears to be the basis of all the other salts of cobalt.

COCCOLITE. See AUGIE.

COLD. (Artificial.)

A new and very curious application of the principle of producing cold by evaporation has been discovered by Profes or Leslie. It consists in placing under the receiver of an air-pump two vessels, one containing a considerable quantity of concentrated sulphuric acid, or of muriat of lime, or of any other substance which absorbs moisture from the air, and the other vessel holding a small portion of water. As soon as the receiver is exhausted, the water begins to boil, though at a common temperature, and when a pretty good vacuum is made, the pumping may be stopped, and after a while the water becomes entirely frozen. For this experiment to succeed, the surface of the substance that absorbs the aqueous vapour, should be considerable, and concentrated sulphuric acid is preferred by Mr. Leslie to any other absorbent of moisture. The water to be frozen must be in small quantity, and contained in a thin metallic dish.

The experiment may be easily performed in the small way in a common air-pump, in the following manner: put into a wide glass tumbler six or eight ounces of good sulphuric acid, set this on the pump plate, lay a little support of wire over the top of the tumbler, and set upon it a thin metallic vessel, holding two or three teaspoonfuls of water; cover the whole with the receiver, and work the pump till a considerable vacuum is made, and the gage is stationary, then let the whole remain for many minutes, and the water will gradually congeal till it is perfectly solid. If this is allowed to remain undisturbed, the vacuum being kept up by an occasional stroke of the pump, the ice gradually becomes rounded at the edges, porous, and insensibly shrinks in every dimension till it totally disappears, leaving only a little trace of whatever saline or earthy impurity the water may contain. Three or four hours will elapse, even in the heat of summer, before the ice of one or two drams of water thus frozen will be totally dissipated, and not the least appearance of melting is observed the whole time.

In this most striking experiment, the first

<sup>b</sup> Ann. Chim. tom. 60.

effect of the exhaustion of the air is to cause the evaporation of a portion of the water, which is instantly absorbed by the sulphuric acid. This produces a fresh vacuum, which is again filled by fresh aqueous vapour, and this is again condensed by the acid; so that this alternate formation of vapour from the water, and absorption of it by the acid, continues as long as any portion of water remains either in the liquid or solid state, provided the acid is not too much diluted to retain its absorbing power.

The temperature of the acid rather increases during this process, both from the condensation of vapour, and from the heat generated by the addition of water to the sulphuric acid. On this account it is of advantage to remove the water to be frozen as far distant as possible from the sulphuric acid. This acid absorbs moisture rapidly till it has gained about its own bulk of water.

Dr. Wollaston has contrived a very simple and striking application of this experiment. The instrument is the same as the common toy, called the pulse-glass, and consists of a glass tube with a bore of about  $\frac{1}{8}$  of an inch in diameter, terminated at each end by a hollow ball, about an inch in diameter, and bent in a right angle at the distance of half an inch from each ball.<sup>a</sup> The length of the tube intervening between each ball is immaterial to the experiment, and may be very considerable. One of these balls should be half filled with water, and the remaining cavity should be as perfect a vacuum as possible. The instrument being thus prepared, let the empty bulb be immersed in a mixture of salt and snow, and the water in the other ball (though the intervening length of tube be two or three feet) will be frozen solid in a very few minutes. The reason of this is, that the vapour of water contained in the empty ball is first totally condensed by the effect of the freezing mixture, and the vacuum thus produced gives opportunity for a fresh quantity of water to be evaporated from the half-filled ball with proportional diminution of its temperature, which in its turn is condensed, till sufficient vapour has been produced to bring the water that furnishes it, below the freezing point and to solidify it. The freezing mixture therefore in this instance has a similar effect with the sulphuric acid in Mr. Leslie's experiment.

Dr. Wollaston has given to this instrument the name of *Cryophorus*, or *Frost-bearer*.

<sup>a</sup> Phil. Trans. for 1813.

### COLUMBIUM.

In a paper by Dr. Wollaston,<sup>b</sup> in the philosophical transactions, the identity of columbium and tantalum is very satisfactorily pointed out. In external appearance, columbite and tantalite bear a very close analogy to each other, except that the sp. gr. of the former is 5.91, while that of the latter is 7.95.

Five grains of columbite being fused for a few minutes with 25 grains of carbonated potash and 10 grains of borax, produced a deep green saline mass, which by the action of dilute muriatic acid was dissolved, with the exception of a portion of white oxyd, which after ignition weighed 4 grs. The muriatic solution being neutralized with carbonate of ammonia, afforded with succinate of ammonia a precipitate, from which by ignition were obtained  $\frac{1}{4}$  of a grain of oxyd of iron. Lastly, prussiate of potash threw down prussiate of manganese, yielding by calcination  $\frac{1}{4}$  of a grain of oxyd.

An equal weight of tantalite afforded by similar treatment

$4\frac{1}{4}$	grains of white oxyd
$\frac{1}{2}$	oxyd of iron
$\frac{1}{10}$	oxyd of manganese
<hr style="width: 20%; margin: 0 auto;"/>	

4.95

Both the white oxyds are nearly insoluble in any of the three mineral acids. In potash, either caustic or carbonated, they are readily soluble, one part of oxyd requiring about eight parts of the latter salt. The alkaline solution may be decomposed by means of any acid, and the recent precipitate, though not soluble in the mineral acids, is completely taken up by oxalic, tartaric, or citric acids.

Neither infusion of galls, prussiate of potash, or hydrosulphuret of potash occasion any change in the alkaline solution, but if this latter be saturated by an acid, the addition of tincture of galls occasions an orange precipitate: this precipitate is again soluble in either of the three vegetable acids already mentioned, as well as in pure ammonia, though the mild volatile alkali appears to have no such effect.

### COPPER.

#### § 1. Ores of

Emerald copper ore. Kopperschmaragd, W. Cuivre Diopside, H.

Its colour is emerald green. It occurs crystallized in prismatic rhomboidal dodecahedrons, which exhibit a triple cleavage parallel to the

<sup>b</sup> Phil. Trans. 1809, p. 246.

sides of an obtuse rhomboid, the alternate angles of which are  $123^{\circ}.58'$  and  $56^{\circ}.2'$ . The lateral planes of the crystals are smooth, and both externally and internally are shining with a vitreous lustre. It is more or less translucent, and scratches glass with difficulty. Sp. gr. 3.3.

Before the blowpipe it becomes of a chestnut brown, and communicates to the flame a yellowish green colour, but does not melt; with borax it affords a globule of copper.

From an examination by Vauquelin of a small portion, scarcely equal to 4 grains, it appears to consist of

Silex . . . . .	28.57
Oxyd of Copper . . .	28.57
Carbonate of Lime . .	42.85
	<hr/>
	99.99

It occurs in Siberia, accompanied by malachite.

Some additional facts and experiments on the sulphuret and oxyds of copper will be found in the article *Affinity* of this appendix.

CRYOPHORUS. See COLD (Artificial).

## D

## DATHOLITE.

The only crystalline form of this mineral as yet known is a strait ten-sided prism, of which two opposite solid angles adjacent to each base are replaced by triangular facets. The colour is greyish-white and translucent: the hardness of the crystals exceeds that of fluor spar. The fragments when exposed to the flame of a candle become of an opaque white, and may then be easily rubbed down between the fingers. According to an analysis by Klaproth it is composed of

35.5 Lime
36.5 Silex
24. Boracic acid
4. Water

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100.0

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It occurs in the neighbourhood of Arendahl in Norway.

Var 1. Externally redish, internally grey; botryoidal; texture, concentric lamellar with very fine divergent fibres; fracture splintery.

Occurs also at Arendahl.

## DIALLAGE.

Under this new species of M. Haüy are included the Schiller spar, regarded by Werner as crystallized serpentine, resplendent Hornblende, remarkable for its brilliant pseudo-metallic lustre, Bronzite usually ranked as a variety of the foregoing, and that variety of Actynolite to which Karsten has given the name of Smaragdite.

The crystallographical character of the species is, natural divisions parallel to the sides of a rhomboidal prism, the obtuse angles of which are a few degrees larger than a right angle, the prism hence resulting being still further di-

visible parallel to the two diagonals of the base. The three varieties belonging to this species are,

1. Diallage verte, or Smaragdite, consisting according to Vauquelin of

50 Silex
21 Alumine
13 Lime
6 Magnesia

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90

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with a variable proportion of the oxyds of chrome and of iron.

2. Diallage Metalloide. Schiller spar, Bronzite, resplendent Hornblende: of which the Schiller spar has been analyzed by Drappier and the Bronzite by Klaproth, with the following results.

S.		B.	
41.	—	60.	Silex
3.	—	0.	Alumine
1.	—	0.	Lime
29.	—	27.5	Magnesia
14.	—	10.5	Oxyd of iron
10.	—	0.5	Water
	<hr/>		<hr/>
98.		98.5	

3. Diallage submetalloide.

Of a dark brown colour, with a slight semi-metallic tinge of violet.

DIAMOND. See CARBON.

## DIASPORE.

The colour of this mineral is ash-grey with a moderately bright lustre between vitreous and resinous: it is composed of slightly curved lamellar concretions easily separable from each other. It exhibits natural joints parallel to the

faces of a rhomboidal prism, the angles of which are alternately  $130^{\circ}$  and  $50^{\circ}$ . Its hardness is somewhat superior to that of glass. Sp. gr. 3.4.

A small portion of this mineral when exposed for a few seconds to the flame of a candle is dispersed in fragments with a brisk decrepitation. If heated in a close crucible it assumes the appearance of boracic acid. It is composed, according to Vauquelin, of

80. Alumine  
17. Water  
3. Oxyd of iron

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100.

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Its gangue is a ferruginous clay.

Is not this mineral a mere variety of the WAVELLITE, first discovered by Dr. Wavel near Barnstaple in Devonshire, and since found in Brazil by Mr. Mawe?

DICHRÖITE. See IOLITE.

DIOPHASE. See COPPER.

DYEING. MORDANTS.

An enquiry of considerable extent and apparently conducted with much pains on the mode in which some of the most usual mordants unite with animal and vegetable fibre has been made by Messrs. Thenard and Roard, of which we shall give a short abstract.\*

*Of Alum Mordants.*

When wool or other fibre is macerated with a solution of alum, either with or without other additions, this salt is commonly considered to be decomposed, the alumine alone remaining united with the animal or vegetable fibre, and thus serving as an intermede for the fixation of the colouring matter. The fact of this supposed decomposition was first examined.

Some silk, thoroughly cleansed and washed, was digested for six days at a common temperature with a solution of 100 grammes of alum in 4 litres of water. It was then taken out and washed in distilled water; the remaining liquor with the washings being then evaporated, yielded pure crystals of alum to the very last. The silk itself was then boiled with twelve successive portions of water, all of which were also evaporated, and gave nothing but pure alum. The entire quantity of alum thus recovered from the silk and from the remaining solution was within  $\frac{1}{20}$  of the quantity of alum originally employed. The silk thus deprived of alum had no greater power of fixing dyes than if the alum-bath had never been used.

From this it is inferred that alum is not decomposed in the fibres of the silk.

Some wool was boiled repeatedly with weak muriatic acid to separate the carbonat of lime which naturally adheres to it. It was then boiled with many portions of fresh distilled water till no trace either of muriatic acid or of lime was left in the washings, (which was a very long and tedious operation) and the wool was left quite pure. Some of it was then boiled in a hot solution of a given quantity of alum, and thus prepared it took colouring matter with great ease. But after being repeatedly boiled in water, all the alum was washed out and most of this salt was recovered in the same state in which it was at first employed, though some of it remained mixed with an animal matter extracted from the wool, and could hardly be made to crystallize. The experiment was therefore repeated with the difference of using a cold alum-bath in the first instance, and then, by successive washing, the whole of the alum to  $\frac{1}{100}$ th part was recovered in crystals unaltered. Alum therefore combines with pure wool without undergoing any change or decomposition.

Cotton and thread gave similar results, only that the subsequent extraction of the alum was much less difficult, as the union between alum and vegetable fibre is much weaker than with animal fibre.

The authors then examined the operation of the alum-bath on wool in its common state and not previously purified of the carbonat of lime which adheres to it. In all the common processes of aluming wool the alum liquor in which it is steeped becomes very turbid, and on cooling lets fall an abundant white precipitate. This was found to consist of sulphat of lime, of neutral sulphat of alumine, and sometimes of a little alumine. The clear liquor above the precipitate, on the other hand, contained alum and acid sulphate of potash with a little animal matter. The wool itself when boiled with water gave up merely alum with a very trifling proportion of this white precipitate. As this precipitate never appears when the wool has been carefully purified from the carbonat of lime, the authors examined the operation of this earth upon alum alone. Alum long boiled with carbonat of lime is totally decomposed by a sufficient proportion of it, into a solution of acid sulphat of lime and a deposit of sulphat of lime with subsulphat of alumine and potash.

Other earthy or alkaline salts have a similar

\* An. Chim. tom. 74.



operation upon alum in changing it to a very acid sulphat of potash or ammonia, and an insoluble sulphat of alumine with potash and the earthy or alkaline matter employed.

Acetite of alumine also unites with animal or vegetable fibre at first without being decomposed, but by exposure to the air some of the acetic acid flies off, in consequence of which a *sub-acetite* of alumine remains in the fibre, together with a little mere alumine.

#### *Cream of Tartar on Wool.*

Some wool, prepared in the way already described, was macerated in a bath of very pure cream of tartar and then washed repeatedly in boiling water. About three-fourths of the cream of tartar used were recovered unchanged, and with it was some neutral tartrate of potash. The washings of the wool were strongly acid, and yielded a very little cream of tartar and a very acid compound of tartareous acid and animal matter. From this and the former experiments may be inferred the effect of wool upon the common mixed mordant of cream of tartar and alum, (since Berthollet has shewn that these salts do not decompose each other) the wool absorbs the alum totally, and a little of the cream of tartar unchanged, but a much greater part enters the wool with great excess of tartareous acid, and of course the liquor in which the wool is macerated contains a portion of the tartar with deficiency of acid, or in other words, as neutral tartrate of potash.

This was further proved by direct experiment. Wool was macerated in a bath of  $\frac{1}{4}$  of its weight of alum and  $\frac{1}{16}$  of cream of tartar: the remaining liquor gave alum, cream of tartar and a mixture of tartrate of potash and animal matter; and the wool itself when long boiled in pure water gave out an atom of cream of tartar and a quantity of a compound of tartareous acid, alum and animal matter. Hence the practical advantage of a compound alum and tartar mordant in cochineal, kermes and madder colours, where the tint is to be enlivened by an excess of acid in the mordant; and on the other hand this compound mordant should be avoided and alum alone employed, with weld, logwood and Brazil-wood dyes, that are degraded by acids.

Some trial was made of simple acids instead of alum as mordants. Wool boiled with a small portion of sulphuric, nitric, muriatic and tartareous acids appeared to take cochineal and madder colours as easily, and to exhibit as great a body of colour as with the alum mordant.

But the supertartrate of alumine appeared to fix a brighter tone of colour than any other mordant. With regard to the quantity of mordant no advantage was gained by increasing it beyond a quarter of the weight of the stuff, nor by prolonging its maceration in the mordant beyond two hours.

#### *Scarlet Dye.*

This dye is usually produced on wool by macerating it with certain proportions of cochineal, cream of tartar, and a highly oxydated and acid solution of tin, in two successive operations. The precise effect of these two mordants was examined in the following way. Some cream of tartar and nitro-muriat of tin were mixed together, and a precipitate separated, which when washed and separately examined shewed the presence of tartareous acid, of oxyd of tin, and of a large excess of muriatic acid. The mother liquor contained cream of tartar, tartrate of potash, and a very acid muriat of tin, together with much of the last mentioned precipitate, but held in solution by the excess of acid. Some very pure wool was first steeped in the usual compound mordant of tartar and solution of tin, and then boiled many times with fresh water, which finally extracted the whole of the mordant which it had imbibed, apparently not differing from the precipitate formed by mixing the materials of the mordant solely. The fine cochineal scarlet therefore is a compound of wool, colouring matter, acid of tartar, muriatic acid and peroxyd of tin. Nevertheless the mordant liquor in which the precipitate is formed is essential towards bringing out the colour, which is done (as the authors conjecture) by its great acidity.

The tartrate of tin (obtained by tartrate of potash or soda and muriated peroxyd of tin) dissolved in muriatic acid, answers as well as the common mordant of cream of tartar and solution of tin.

The scarlet dye is not quite firmly fixed into the wool by any of the processes, hence it may be gradually washed out by repeated maceration in warm water, till no other hue remains on the wool than a pale flesh-colour.

The researches of these chemists are evidently imperfect, but the main points which they mean to establish are, the combination of alum with animal fibre without any decomposition of the alum, and the change in the tartar solely, by which its acid is fixed on the cloth; and likewise the powerful effect of the colouring matter to fix the mordant on the ani-

mal fibre, which is no less powerful than the action of the mordant as an intermede for colouring matter.

*Acctite of Alumine.*

Some valuable remarks on this salt, which is so largely used by the calico-printers, will be found under the article ACETIC ACID in this Appendix.

## E

ETHER. See ALCOHOL.

EUCHLORINE. See MURIATIC ACID.

## F

FERMENTATION. See ALCOHOL.

FETTSTEIN. Pierre grasse, H.

The colour of this mineral is a deep greenish-grey; it occurs crystallized and amorphous, and presents natural joints parallel to the faces of a strait rhomboidal prism and also parallel to the short diagonals of the bases. Its fracture is uneven, with a greasy lustre and slightly chatoyant. It scratches glass and gives sparks with steel. Sp. gr. 2.61.

It is easily fusible before the blowpipe into a white enamel, and is composed, according to Vauquelin of

44.	Silex
34.	Alumine
4.	Oxyd of iron
0.12	Lime
16.5	Soda and potash (the former
	being in the greatest
98.62	proportion.)

It has hitherto been found only in Norway.

FLUORIC ACID. FLUOR SPAR. A very valuable memoir on this acid has been published by Messrs. Gay Lussac and Thenard,<sup>a</sup> who have discovered some very curious circumstances relative to this singular acid.

The reader will find it stated (*Chem. Dict. Art. Fluoric Acid*) that fluoric acid prepared from fluor spar, and distilled with sulphuric acid, always carries with it a portion of the silex of the glass when prepared in glass retorts, and therefore that the only way to avoid the presence of this earth, was to select a pure fluor spar and to employ leaden vessels. This way however has been thought to introduce a different impurity, namely, a portion of the lead of the vessel used, but the authors of the present memoir scarcely allow of this. Previous to the researches of these eminent chemists the fluoric acid had only been obtained in a dilute state, the distilled acid being received in water, but the present memoir makes us for the first

time acquainted with *pure concentrated liquid Fluoric acid*. It is prepared in the following way.

The apparatus consists of three leaden tubes, which must be made without any solder and ground to fit as well as possible: the tube A. (Plate, Fig. 5) contains the fluor spar and sulphuric acid: the bent tube B. conducts the distilled acid into the tube receiver C. set in a vessel of ice. Select some very pure fluor spar quite free from any crust of quartz which often covers this mineral, reduce it to fine powder and put it with about twice its weight of concentrated sulphuric acid into the tube A, which is set in a small furnace, and stir the materials well with an iron or copper rod. Lute all the joinings carefully with fat lute (for the lead can never be made to fit close enough by mere grinding) and then heat the tube very gradually, which must not be above two-thirds full. Soon a boiling will be heard, and the pure fluoric acid will pass through the conducting tube B. to the receiver C. where it will condense into the liquid acid. The operation is finished when on detaching a little the conducting tube from the receiver, the end of the former is no longer moist. Besides applying the heat gradually and very moderately, it is of use not to keep it up longer than necessary, as the sulphat of lime sticks very closely to the leaden tube and cannot be got off without difficulty. Instead of the above simple apparatus, some chemists use with equal success a leaden retort (made of two pieces fitting to each other for greater convenience) and the beak fitted to a leaden receiver.

Before we mention the chemical properties of this acid, we shall notice by way of precaution the excessive caustic property which it possesses in destroying all animal matter. The instant that a drop of the concentrated acid touches the skin it destroys the surface, a violent pain soon follows, the adjacent parts be-

<sup>a</sup> Recherches, tom. 2.

come white and painful, and a deep boil or slough is produced in the flesh, forming a sore which takes several days or even weeks to heal, and even endangers the whole finger if the quantity of acid amounts to some drops.

A single instant of contact of the concentrated acid appears sufficient to produce the mischief, which will take place several hours after the time of contact; so that chemists who repeat these experiments should take particular care to avoid these accidents when replacing the lute, pouring out the acid, &c.

The concentrated Fluoric Acid thus obtained is a liquid at any temperature from  $-4^{\circ}$  Fahr. to  $60^{\circ}$ . The heat at which it boils is not ascertained, but it is certainly easily evaporable, especially when in contact with air; for thus exposed, it soon wastes away at a very moderate heat. It is difficult to find proper vessels to keep this powerful substance. Glass vessels of course are improper, as the acid instantly corrodes them; and many of the metals are also acted on by it. Leaden vessels would answer very well if it were not for the difficulty of making any leaden stopper to fit properly without the assistance of lute, which itself is gradually altered by the acid vapour. The authors of this memoir prefer silver vessels.

As soon as the concentrated fluoric acid is exposed to the air it absorbs the atmospherical moisture, and in so doing emits abundance of strong suffocating vapours, which should be carefully avoided. When a few drops of the acid are added to water much heat is produced and a noise like that of quenching red-hot iron; in which respect it resembles and is even superior to, the strongest sulphuric acid.

The moment this fluoric acid touches glass it takes off its polish, the acid heats, boils, and totally disappears, resolving itself into silicated fluoric acid gas, exactly similar to that produced by distilling fluor-spar and sulphuric acid from glass vessels. This may be shewn in a striking manner by distilling the pure acid from a vessel as above described, but instead of using a leaden receiver causing the conducting leaden tube (previously dipped in melted wax to protect it from the action of mercury) to pass under a glass jar full of mercury and inverted over this fluid. As soon as a drop of the strong liquid acid touches the inner part of the glass receiver it attacks the glass, makes it opaque, and the acid is speedily converted into vapour along with the silix of the decomposed spot of glass, which is shewn by its displacing an equivalent volume of the mercury with which the tube

was filled. There remains on the glass a solid matter composed of acid fluat of silix with a little of the wax. Though this silicated gas is formed almost instantaneously, it appears to be as fully saturated with silix as that procured by the slow distillation of fluor-spar, glass, and sulphuric acid. Fluoric acid therefore when pure is in a liquid state, however concentrated, if the temperature does not exceed about  $60^{\circ}$ , but its union with silix enables it to assume the form of a permanently elastic gas at any temperature, which however is absorbed and decomposed by water, as will be presently mentioned.

When the pure fluoric acid is diluted with so little water as still to emit fumes in the air, its action on silix is still instantaneous, and it equally retains the property of resolving itself by this action into silicated fluoric gas; but when further diluted, this latter property ceases, and its action on glass is proportionably weakened and retarded. It is more conveniently employed in its diluted state for etching on glass, when its action is not apparent till after some hours.

A similar use of this acid is to destroy the polish of glass, which may be advantageously employed for lamp-shades.

When the sole object is to prepare a dilute acid, it will be done with much more convenience by distilling the pure fluor-spar and sulphuric acid in leaden vessels and receiving the product in a leaden vessel containing water.

Pure liquid fluoric acid acts with prodigious vehemence on potassium when a piece of this latter is dropped into the acid. A violent detonation takes place, so as to disperse the whole contents; but when the acid is gradually applied to the potassium enclosed in a tube full of azotic gas, the action is more moderate, and the products can be collected. They are, chiefly, a very large quantity of hydrogen gas, and a transparent liquid, which soon crystallizes in the air into *acid fluat* of potash. Hence the authors conclude that the most concentrated fluoric acid contains a portion of water, that when this unites with potassium the water is decomposed, its hydrogen appears in its simple form, and its oxygen converts the potassium to potash, which then unites with the acid into fluat of potash. If this explanation be just, the potassium does not decompose the fluoric acid, but only the water with which it is united, when liquid.

*Alkaline and Earthy Fluats.* Neutral fluat of potash was made by direct combination of

the acid and alkali. This neutral salt is very deliquescent, has a pungent taste, and is not easily crystallized. Sulphuric acid decomposes it even when cold, with much effervescence and disengagement of vapour. Lime-water, strontian and barytic water, and the neutral solutions of barytes, strontian, lime, magnesia, alumine, glucine, yttria, and zircon, when poured into a solution of fluat of potash, all produce a precipitate of the fluoric acid and the base employed.

When silicated fluoric acid gas is passed into water a copious precipitate takes place, which consists of an acidulous fluat of silex, and there remains in solution a very acid fluat of the same earth. If caustic potash is added to the latter solution, a nearly insoluble salt is formed, which is a triple compound of fluoric acid in a little excess, of potash and of silex. So nearly is this salt insoluble that the supernatant liquid scarcely leaves any residue when evaporated to dryness. This triple salt is in the form of a transparent jelly, nearly tasteless, but reddens litmus, and may be dried without decomposition. At a red heat and also by sulphuric acid in the cold it is decomposed, and gives out common silicated fluoric gas. An excess of alkaline solution dissolves this triple salt if heated.

Soda combined directly with pure fluoric acid, forms a hard salt in small crystals, which is somewhat more soluble in hot than in cold water. It neither deliquesces nor effloresces. Sulphuric acid decomposes it with strong effervescence of fluoric acid gas. The simple solutions of the earths and also the soluble earthy salts form insoluble precipitates with this salt, consisting of the fluoric acid and the base employed.

Soda appears to act upon silicated fluoric acid in a very different manner from potash, for instead of only partially decomposing this compound, and forming triple silicated salts, it totally separates the silex, when at a boiling heat, in a gelatinous form, and the liquor separable by filtration is pure fluat of soda, not differing from the salt made by the direct union of the pure acid and soda.

Fluat of ammonia formed by the pure acid and liquid ammonia, though neutral at first, becomes acidulous by evaporation, part of the alkali volatilizing, and then is incapable of crystallizing, and finally evaporates totally in white fumes. When liquid ammonia is added in excess to silicated fluoric acid, much of the silex separates as a white opaque jelly, and is the

pure earth uncombined with any portion of acid. The supernatant liquor is a triple compound of fluoric acid, silex, and ammonia, which becomes acidulous by evaporation, and then a fresh addition of ammonia separates more silex; and this alternate evaporation of excess of ammonia and precipitation by fresh alkali, may be repeated a number of times on the same materials. Hence the fluat of ammonia can only be made by the direct union of the pure acid and ammonia; but pure silex may be extracted from the silicated fluoric acid by means of this alkali.

Pure fluoric acid causes a flocculent precipitate in barytic water, which an excess of the same acid or of the nitric or muriatic acids, will redissolve. The same barytic fluat is produced by adding fluat of potash or soda to any soluble salt of barytes. But when any of these barytic salts is added to the silicated fluoric acid, after some minutes, a quantity of very hard small crystals falls down, which are insoluble in water or acids, and are a triple salt of fluoric acid, barytes, and silex.

The compound salt of fluat of silex and fluat of lime, or triple compound of fluoric acid and these two earths, probably exists native, for there are many specimens of fluor spar which appear quite uniform and transparent, but yet give the silicated fluoric acid, and not the pure acid, when distilled.

Fluoric acid diluted with six or seven parts of water dissolves zinc rapidly, and with disengagement of much hydrogen. The solution at first remains clear owing to the excess of acid, but after a time the fluat of zinc separates almost totally in white flocculi. The same salt is made immediately by adding fluat of potash to sulphat of zinc. This fluat is tasteless, insoluble in water, but readily dissolves in nitric, muriatic, or its own acid. It cannot be crystallized.

The habitudes of iron with fluoric acid much resemble those of zinc, only the fluat of iron is much less easily soluble in an excess of its own acid.

Fluoric acid moderately concentrated, does not act upon metallic tin cold or hot, but it readily dissolves the peroxyd of this metal. This salt may be evaporated to dryness without being sublimed, in which it differs from the muriat of tin.

The suboxyd of tin is also soluble with ease in fluoric acid. When evaporated by itself with contact of air, it becomes oxygenated, and is changed to the last-mentioned salt; but evapo-

rated in contact with tin filings, it remains unchanged, and very brilliant white acid crystals of fluated suboxyd of tin are formed.

Metallic copper is not attacked by fluoric acid, even with only twice its weight of water, but the oxyd of copper easily dissolves, and small blue acid crystals are produced.

Fluoric acid easily dissolves the oxyd of silver, and the salt has a very strong metallic taste, is highly soluble in water and deliquescent. It is not volatile by heat, but fuses like luna cornea, losing thereby its excess of acid, but remains soluble. It cannot be crystallized. It stains the skin black. The fixed alkalies and earths decompose it, but not ammonia. Metallic silver is not acted on by this acid, but it is readily dissolved by heating fluated peroxyd of mercury with silver. Fluat of potash does not precipitate nitrat of silver.

Lead is only acted on by fluoric acid when oxydated. Fluat of lead is readily formed by fluat of potash and acetite of lead. It precipitates in white flocculi, which become brilliant laminae after washing. It is insoluble in water, but readily dissolves in nitric, muriatic, or fluoric acids. It melts at a low red heat, and turns yellow, losing part of its acid.

Metallic mercury resists fluoric acid, but the red oxyd dissolves in it when moderately diluted and boiled in a platina vessel. This salt is in small yellow lamellar crystals, but it forms with difficulty, and requires a great quantity of the acid. These crystals totally exhale when strongly heated. They are acid, but, when washed with water, a part of the salt dissolves along with most of the excess of acid, and the remaining salt becomes of a deep orange or red. In this separation by water into a soluble acid salt, and an insoluble neutral salt, the fluat of mercury agrees with most of the other highly oxydated mercurial salts.

The authors of this interesting memoir then proceed to describe other properties of the fluoric acid, and in particular a very singular compound of this with the boracic acid which they have discovered, and to which they give the name of *Fluoboracic acid*. But before we proceed with this part of the subject, we shall notice a valuable paper on many of the properties and compounds of fluoric acid by Mr. J. Davy, whose experiments appear to have been made nearly at the same time with those of the French chemists above described, though not published so soon.<sup>b</sup>

Pure fluoric acid, as Mr. J. Davy observes,

has never yet been obtained in a gaseous state, and only two substances have hitherto been known to have the power of uniting with it into a permanently elastic gas, namely, silex and boracic acid. The former substance makes the well known compound first discovered by Scheele, and to which the term *Silicated Fluoric Gas* is properly applied. It is difficult, as already mentioned, to avoid obtaining this gas in treating fluor spar with sulphuric acid, unless a very pure fluor be chosen and metallic vessels used. It is conveniently prepared by adding pounded glass to the spar and acid, and by this means the glass retort may be saved for a future operation. This gas is perfectly saturated with silex, for it may be long kept under glass vessels without taking off their polish. A hundred cubic inches of this gas at a medium pressure and temperature, weigh 110.78 grains, or about three times as much as common air, of which 100 cubic inches in similar circumstances weigh 36.45 grains.

To analyze silicated fluoric gas, Mr. J. Davy caused 40 cubic inches of it to be absorbed by liquid ammonia, and obtained from it 27.2 grains of pure silex, after fulledulcoration and ignition. Supposing the remaining weight of the 40 cubic inches to be fluoric acid, (and therefore the whole of the silex to have been separated by the ammonia) it would amount to 17.1 grains, and hence silicated fluoric gas would contain

61.4 Silex
38.6 Fluoric acid
-----
100.0

This gas is partially and unequally decomposed, by the action of water, into a precipitate of much silex and a little acid, and a liquid containing much acid and little silex. This liquid is properly termed by Mr. D. *Subsilicated Fluoric Acid*. To analyze it, Mr. D. assumes that the precipitate formed by the absorption of silicated fluoric gas in water, is mere silex, and that the whole of the acid remains in the solution, (which is contrary to the opinion of Gay Lussac) and hence the *Subsilicated Fluoric Acid* differs from the former only by the quantity of silex separated on its absorption by water. It is therefore thus composed.

54.56 Silex
45.44 Acid
-----
100.00

<sup>b</sup> Phil. Trans. for 1812, part 2.

Water, Mr. D. finds, will absorb and decompose about 263 times its bulk of silicated fluoric gas by direct experiment. Dr. Priestley found that when muriatic gas is admitted to water that has absorbed the fluoric gas, the former is totally absorbed, and the latter resumes its original gaseous state, taking up with it the silex which had been separated by the water. The liquid that remains is simple muriatic acid. Sulphuric acid has the same effect as the muriatic in expelling silicated acid from water by which it had been absorbed. In either case, much effervescence takes place in proportion as the silicated gas resumes its gaseous form.

The liquid subsilicated acid does not appear to corrode glass vessels in which it is kept.

Silicated fluoric gas, like carbonic gas, condenses twice its volume of ammoniacal gas when the two are mixed over mercury: and they unite only in these proportions, whatever excess of either gas be employed. The result is a dry salt, containing according to Mr. Davy, 24.5 per cent. of ammonia, and saturated with silex: this salt is decomposed by water as the silicated fluoric gas is, the same proportion of silex being separated, and the liquid residue being a subsilicated fluat of ammonia, of which the alkali amounts to 28.34 per cent. This salt, obtained by slow evaporation, is in the form of brilliant tetrahedral prisms, very soluble in water but not deliquescent, and subliming unaltered by heat. It just reddens litmus. Mr. Davy observes, that if the concentrated solution of this salt is evaporated in glass or earthen vessels, it powerfully erodes them if heated to the boiling point, as is shewn by a deposition of silex on dilution with more water.

The sulphuric acid decomposes the subsilicated fluat of ammonia, expelling silicated fluoric gas. Potash also decomposes it, expelling the ammonia, and forming subsilicated fluat of potash.

Contrary to the experience of Messrs. Gay Lussac and Thenard, Mr. J. Davy finds that an excess of ammonia separates the whole of the silex from the subsilicated fluat of ammonia, and the remaining liquid furnishes by evaporation in metallic vessels a simple fluat of ammonia, containing 76.4 of alkali, and 23.6 of pure fluoric acid, besides water of crystallization. This fluat thus formed is quite neutral, and deliquesces in the air. When heated somewhat above the boiling-water point, a part of the ammonia flies off, leaving a salt with excess of acid behind. When the heat is further raised, the whole salt sublimes in very pungent fumes,

highly dangerous to respire. If this be done in a glass vessel it is strongly corroded, and the salt is now converted to silicated fluat. Indeed the action of this simple fluat of ammonia is so strong on glass, that a little of the solution pencilled on and moderately warmed, will speedily produce an etching.

#### FLUOBORACIC ACID.

This name has been given by the discoverers, Messrs. Gay Lussac and Thenard, to a singular gaseous acid, a compound of the fluoric and boracic. These chemists finding that the pure fluoric acid, obtained from fluor spar and sulphuric acid in the manner described in the foregoing article, though a highly concentrated liquid, was probably combined with a portion of water (as concentrated sulphuric acid itself is) endeavoured to expell the fluoric acid pure, dry and gaseous, from fluor spar by the action of another acid, which could not be suspected to contain any water in its composition. The vitrified boracic acid was selected for that purpose, and on distilling it in a strong heat with fluor spar, it was found that the fluoric acid was indeed expelled in a perfectly dry state, but that in the process it became united chemically with a portion of boracic acid, which it thus volatilized, and retained as a permanently elastic gas, in the same manner as silex is gassified with fluoric acid when fluor spar, glass and sulphuric acid are distilled together.

Therefore, though these ingenious chemists failed in their object of producing a pure gaseous fluoric acid, they have discovered a new gaseous compound of fluoric and boracic acids, which has several remarkable properties.

The fluoboracic acid is thus prepared. Take the lower end of a gun-barrel with the touch-hole plugged up, coat it with good fire lute, put into it a quantity of very pure fluor spar mixed with half its weight of pure vitrified boracic acid, both reduced to powder; lute on the end of the barrel a bent glass tube; put the barrel into a furnace so that the open end projects, and let the extremity of the glass tube dip under a jar full of mercury. When the heat is raised to full redness, the acid gas is expelled in dense vapours, and as soon as they are totally absorbable by water, the gas is pure and may be collected under mercury.

This compound acid gas is a colourless permanently elastic fluid; its smell is pungent; it extinguishes light instantly, and powerfully reddens blue vegetable colours. When this gas comes in contact with any air containing hygrometric moisture, it condenses in thick white

fumes, but it mixes uniformly with dry air, and hence it is an excellent test of hygrometric moisture. It has no action whatever on glass. It corrodes vegetable and animal matters as powerfully as the strongest sulphuric acid, and carbonizes them, so that it instantly blackens paper.

It converts alcohol into ether. It does not however corrode the skin whilst experiments are made upon it. Water appears to dissolve at least as much of this gas as of muriatic acid gas, and at the same time the water heats and expands much.

When it is saturated it forms a limpid fuming caustic liquid, which when heated will give out only a fifth of the gas that it had absorbed, and it then resembles strong sulphuric acid in causticity and in appearance, and like this acid its boiling point is very high, and when distilled by itself, it condenses in long streaks on the receiver.

The fluoboracic acid combines very easily with the various salifiable bases. When saturated with ammonia and when the solution is evaporated to dryness, a higher heat expels a white sublimate of fluat of ammonia mixed with some borate of ammonia, and pure fused boracic acid remains behind.

These chemists did not pursue the examination of these compounds much further, except to ascertain that the fluoboracic gas is not altered by passing through red-hot iron turnings.

Mr. J. Davy (in the paper above quoted) finds that this compound acid gas may be procured in an easier manner than that just described. It is sufficient to heat gently in a common glass retort, one part by weight of fused boracic acid mixed with 2 parts of fluor spar, both in fine powder, and about 12 of sulphuric acid. Common calcined borax will even answer, but not so well. If the heat is gentle the retort will be untouched, and pure fluoboracic gas will be produced. If the heat be raised higher, a viscid mixture of sulphuric and fluoboracic acid comes over. Not more sulphuric acid should be used than is necessary to decompose the fluor spar, on account of the quantity of the fluoboracic gas which is absorbed by the sulphuric acid. The specific gravity of this gas, Mr. J. Davy estimates to be to that of common air, as 14.7 to 6.2, and hence 100 cubic inches weigh 73.5 grains. Water condenses no less than 700 times its volume of this gas, which is more than of any other known gas. Water thus fully saturated has 1.77 specific gravity. Sulphuric acid condenses about 50 times its volume

of the gas, and forms a dense tenacious compound.

Some singular results take place on combining the fluoboracic gas with ammoniacal gas. When equal volumes of the two gasses are used, they condense into a solid white opaque salt. When a double or triple quantity of ammonia is employed, the dry salt resolves itself into a transparent colourless fluid, though without containing any water.

#### *Decomposition of Fluoboracic and Silicated Fluoric Gas.*

The singular energy of potassium in depriving most oxyds of their oxygen, and leaving their bases separate, has been employed to discover the hitherto unknown radical of fluoric acid. But here a particular difficulty occurs, as no means have yet been found of obtaining fluoric acid free from water, except by combining it with silex or with boracic acid in the form of gas. As the presence of water entirely defeats the purpose of applying potassium, it is necessary to take the other alternative of employing one of the two compound fluoric gasses.

Messrs. Gay Lussac and Thenard have examined the effect of potassium on both these gasses.

Potassium is not sensibly acted on by dry silicated fluoric gas at a common temperature, but if it is melted in the gas by a gentle heat, it thickens and burns strongly with much light and heat. In this process a large quantity of the gas is absorbed, very little hydrogen is given out, and the potassium is converted into a reddish brown substance. When this latter substance is digested with hot water, some hydrogen is given out, the hot water holds in solution some fluat of potash; and the insoluble portion, after calcination in an open crucible or combustion in oxygen, yields a triple fluat of potash and silex. From these facts the authors conclude, that the potassium when burned in silicated fluoric gas, decomposes the fluoric acid, and that the reddish brown substance is a compound of *fluoric radical*, potash, and silex, and perhaps some undecomposed fluoric acid, and hence when it is afterwards digested with water, the fluoric radical returns to the state of fluoric acid, and forms with the potash and silex an insoluble fluat of silex and potash. Potassium burns with great ease in this gas, and when only a small quantity is used, it may be done in a small glass tube full of the gas, into which the potassium is introduced on an iron support, and heat applied externally by a spirit lamp. Sodium

has a similar action on this gas to that of potassium.

Potassium is equally combustible in the fluoroboric gas as in the silicated gas, and nearly with similar appearances. The residue after combustion is chocolate coloured solid unmetallic in appearance, with very little taste and fusible at a cherry red heat. When thrown into water, hot or cold, it gives out only a few bubbles of hydrogen and a portion dissolves. This portion is mere float of potash, for it is precipitated by the watery solutions of lime, barytes, and strontian, and also by the soluble salts of these earths; and moreover when evaporated to dryness, the salt gives much fluoric acid vapour with sulphuric acid, and sulphat of potash is left. On the other hand, the insoluble portion of the product of potassium burnt in fluoroboric gas is a dark coloured insipid infusible substance, which easily decomposes nitric acid, and is thereby converted to *Boracic acid*. It is equally changed to this acid when burnt in the open air or in oxygen gas, and when deflagrated with nitre, it yields borat of potash. From all these circumstances, they conclude that this chocolate-brown insoluble portion is the *Boracic Radical*, or *Boron*, probably combined with a little fluoric radical.

Similar experiments to those just mentioned have been performed by Sir H. Davy,\* with results that correspond in a very great degree. When silicated fluoric acid gas is introduced into a plate-glass retort, exhausted after being filled with hydrogen gas, and potassium is added, white fumes are perceived, and the metal becomes covered with a greyish crust. These do not materially increase while the heat is kept moderate, and no change will be found in the gas, except by the addition of a small quantity of hydrogen. But if the heat be raised to the sublimation of potassium, the metal rises through the crust and kindles, burning with a most brilliant red light. If the potassium is in sufficient

quantity, all the fluoric gas is consumed, and hydrogen alone remains, which does not exceed a tenth of the fluoric gas if previously dried. A chocolate coloured mass is left in the retort. This substance effervesces violently in water, giving out an inflammable gas. When a portion of it is heated in the air, it burns slowly, and even in oxygen with difficulty. The final product of the combustion of this mass and of its solution in water, is float of potash with silex.

The same eminent chemist also employed a fluoric gas free from silex by heating fluor spar and boracic acid in an iron tube, and of course obtained the fluoroboric gas, but in this experiment the gas was decomposed by potassium as soon as formed. The result was a dark brown combustible mass, affording the fluoric and boracic acids after combustion. Hence he infers it to be probably a compound of the two bases of these acids, or rather of their oxyds.

The general inference from all these last related experiments of the action of potassium on the compound fluoric gasses, certainly gives probability to the opinion of the existence of a *Fluoric Base*, or *Radical*, but this base has never been obtained separate, as it is combined, in all probability, with the base of silex in one instance, and the base of boracic acid in the other. Other attempts to insulate the fluoric acid by distilling fluor spar with vitreous phosphoric acid have equally failed, and even were this difficulty surmounted, it would still be not easy to contrive a mode of unexceptionable analysis, owing to the powerful action which this acid exerts on the silex which enters so largely into the composition of every kind of glass vessel.

*Fluor Spar* has been analyzed both by Klaproth and Dr. Thompson. Dr. T. finds no more than  $\frac{1}{60}$  of its weight of water, and the ignited spar contains about 67 $\frac{1}{2}$  per cent of lime, and 32 $\frac{1}{2}$  of acid. Klaproth's analysis gives nearly the same result.

## G

### GABBRONITE.

The colour of this mineral is grey, with different shades of bluish and reddish. It occurs massive; is harder than glass, but does not readily give sparks with steel. It is translucent on the edges; is of a very compact texture, and when broken, exhibits a splintery fracture. Before the blowpipe, it melts with difficulty

into a white opaque globule. It has not as yet been analyzed, but as far as may be judged from external characters, is but little different from compact felspar.

It has hitherto been found only in Norway, accompanied by octohedral iron ore, red compact felspar, hornblende and talc.

\* Phil. Trans. for 1809, p. 85.



## GALLIC ACID.

In our former article we described Scheele's original process for preparing this acid, and also Deyeux's method by sublimation. Mr. Richter has given a different process, by which this acid is prepared in very considerable purity. It is the following.<sup>a</sup> Make a cold infusion of finely powdered gall-nuts in water, frequently stirring it, then strain the whole through a cloth, and press the residue strongly to get out the whole infusion. Evaporate the liquor to dryness with a very gentle heat, which will leave a dark brown brittle mass. Reduce this to a fine powder and digest it with very highly rectified alcohol, added twice successively. The first tincture thus prepared will have a weak straw-colour; the second will be nearly colourless. The undissolved part is tannin almost pure. Mix both the spirituous tinctures, and distill it in a retort till only an eighth part is left. Add water to the residue in the retort and warm it, and then reduce it by evaporation, and small white crystals will separate, as long as any mother liquor remains. These crystals are the Gallic Acid. One pound of galls will give about half an ounce of these crystals.

This acid certainly contains a smaller admixture of tannin than that prepared in Scheele's method; for tannin is scarcely at all soluble in alcohol, whereas gallic acid is highly so, but the alcohol here employed should be very highly rectified. This acid when added to a perfectly clear and neutral solution of sulphat of iron does not produce any change till the iron has absorbed an additional portion of oxygen from the atmosphere. In this respect it differs from Scheele's acid, or from the simple infusion of galls, which immediately gives a purple hue to the neutral sulphat of iron. Richter therefore supposes, with some probability, that the tannin in this case unites with the sulphuric acid, and detaches a portion of oxyd of iron to unite with the gallic acid.

Bouillon La Grange has given a valuable comparative view of the shades of difference in these acids, with some remarks on the intimate nature of gallic acid.<sup>b</sup> Berthollet having proposed the oxyd of tin as a method of freeing the common brown gallic acid from its adhering tannin or extract, La Grange has examined this process, and finds that by evaporating a solution of this brown acid in contact with a certain quantity of the oxyd of tin, and then again diluting with water, the acid still gave a precipitate with animal jelly, though

slightly, and the solution when crystallized furnished a gallic acid of greater purity than before. But on repeating the process with a fresh portion of the oxyd of tin, the solution was now so entirely decomposed as to be clear and colourless, to give no precipitate either with sulphat of iron or with jelly, and to yield no crystallized acid on evaporation.

The red oxyd of mercury when long boiled with the gallic acid, finally decomposes both the pure acid as well as the tannin.

Charcoal recently calcined, when boiled with gallic acid, deprives it of its peculiar taste; gives it a green colour, and takes away its property of precipitating jelly; and a greater proportion of charcoal destroys the acid altogether.

All these experiments shew the impossibility of obtaining gallic acid free from the tannin except by sublimation, but it remains to be shewn whether the sublimed acid is identical with the mere acid part of the crystallized acid. M. La Grange has contrasted the differences between these two acids. The sublimed acid, he observes, has less acidity, it is decomposed in the air, it has no action on barytes, or carbonat of ammonia, or on muriat of tin; the precipitate obtained by nitrat of mercury is blackish instead of being yellow, and that by acetite of lead is yellow and scanty, instead of being white: oxymuriatic acid renders it brown, whereas it does not change the colour of the crystallized acid. The sublimed acid does not precipitate animal jelly.

In continuing these experiments both on the acid and on the gall nut itself, the author uniformly obtained a quantity of acetous acid by the distillation of all these varieties of gallic acid, whence he is led to the conclusion that the acetous acid is the real acid basis of the gallic acid, as well of most other supposed individual vegetable acids, and that its peculiar characters are masked by volatile or fixed empyreumatic oils, by tannin, by extract, or by other vegetable principles with which it is capable of entering into intimate combination.

## GLAUBERITE.

The colour of this mineral is wine yellow of greater or less intensity: it occurs only crystallized, in the form of an oblique prism with rhombic bases. The faces of the base are smooth and brilliant, those of the sides are striated parallel to the edges of the base. It presents natural joints in two directions, namely parallel to the base (and these are the easiest

<sup>a</sup> Ann. Chim. tom. 52.<sup>b</sup> Ann. Chim. tom. 60.

to observe) and inclined upon the former at an angle of  $104^{\circ}$ : in other directions the fracture is vitreous. It is transparent, in hardness between gypsum and calcareous spar. Sp. gr. 2.73.

On immersion in water it becomes opaque, and is the only mineral exhibiting this character. Before the blowpipe it decrepitates, and then melts into a white enamel. It is in part soluble in a moderate quantity of water, and entirely in a large quantity of the same fluid. It appears to contain no water of crystallization, but is composed of

49. sulphate of lime  
51. sulphate of soda

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100

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It occurs at Ocagna, in New Castille, disseminated in rock salt, and was first discovered by M. Brongniart. (*Journ. de Mines,*) xxiii. page 5.

#### GOLD.

A remarkable difficulty attends the analysis of the salts and oxyds of gold, which has not yet been got over in a satisfactory way, though several apparently accurate series of experiments have been undertaken on this subject, particularly of late by several French chemists, now that an attempt has been made to restore gold to its ancient place as an important article of the materia medica.

Two difficulties oppose the accurate estimation of the proportion of oxygen with which gold unites in its salifiable compounds: one of them is that no alkali or single base will precipitate the whole of the oxyd of gold in a given portion of its muriatic solution, and hence the usual way of dissolving a given portion of any metal, and of finding the quantity of oxygen in its oxyd by the increase of weight in the total precipitate over that of the metal employed, cannot be used with the salts of gold: the other difficulty is the readiness with which the oxyds of gold return, either totally or partially, to the metallic state, so that of any given portion of precipitated oxyd, one part will often become reguline in the common way of drying, and thus defeat the purpose of analysis. To these difficulties may be added that of the solubility of the simple oxyd of gold in water, so as to render edulcoration an uncertain operation, and one attended with loss.

We shall add a few particulars concerning

the salts and compounds of gold from Proust,<sup>a</sup> Vauquelin,<sup>b</sup> Duportal<sup>c</sup> and Oberkampff.<sup>d</sup>

The most powerful aqua-regia for dissolving gold, according to Vauquelin, is composed of two parts of muriatic acid to one of nitric acid, both concentrated, and this nitro-muriatic acid will dissolve by boiling about a third of its weight of pure gold. Proust employs a greater proportion of muriatic acid. When the acid has dissolved as much gold as it will take up, the solution is still very acid. If it is evaporated sufficiently, it yields yellow prismatic crystals of muriat of gold, particularly if an excess of gold be kept in the liquor. This muriat is highly deliquescent, becoming fluid in a warm day and solid again in a cold one. The taste is acerb and bitter. When moderately heated, oxymuriatic acid is given out, and the gold remains in the metallic state, but spongy, and without lustre. A part however of the gold is volatilized with the acid.

The action of potash on the solution of gold in nitro-muriatic acid has been examined with peculiar attention. When caustic potash is added to the solution in the cold, it becomes of a deep red, but no turbidness whatever ensues, even on keeping it for a length of time. But if after the solution is saturated with potash it is heated to boiling, a bulky red flocculent precipitate falls down. The supernatant liquor is then colourless, but if it is again supersaturated with muriatic acid it resumes its original yellow colour and will still give a copious precipitate of gold on adding tin, or sulphat of iron. Potash therefore will not separate the whole of the gold, nor probably much more than half of it, as it was found that 72 grains of gold in solution only yielded 40 of the oxyd by adding potash. The reason of this imperfect separation appears to be the great tendency of muriat of gold to form a triple salt with muriat of potash, (and it is the same with the other alkaline or earthy muriats) which triple salt is very soluble, and not further decomposable by any excess of alkali, when the metallic salt does not exceed a certain proportion of the whole. For this reason too, the quantity of precipitate obtainable by potash is in a reverse proportion to that of acid present, so that where the acid is in great excess, no separation will take place on adding any quantity of potash, as the muriat of potash will then be sufficient to hold all the muriat of gold in triple combination.

<sup>a</sup> Journ. de Phys. tom. 62, or Phil. Journ. vol. 14.

<sup>b</sup> Ann. Chim. tom. 77.

<sup>c</sup> Ibid. tom. 78.

<sup>d</sup> Ibid. tom. 80.

If the precipitate by potash is washed and dried in the gentlest heat, it is not however an uniform oxyd of gold, as might be expected, but a portion returns to the metallic state, so that the powder is a mixture of reduced gold and of its oxyd. These however may be separated by pure muriatic acid, which dissolves out the oxyd and leaves the reguline part untouched. The precipitate from the muriat of gold, by potash either caustic or carbonated, appears also by Vauquelin's experiments to carry down with it a portion of muriatic acid, since the washings long continue to curdle nitrat of silver. The oxyd itself indeed is also slightly soluble in hot water even when all the muriatic acid is washed out, so that by a succession of edulcorations by far the greater part of the entire precipitate may be washed away. No carbonic acid appears to enter this precipitate though a carbonated alkali be employed.

The clear liquor remaining after the separation of the oxyd of gold from its muriatic solution by potash, becomes yellow on saturation of the alkali by the same acid, and shews the presence of gold by adding sulphat of iron or tin. When slowly evaporated it yields crystals of simple muriat of potash, (shewn to contain no gold by not turning yellow with muriatic acid) and the triple muriat of potash and gold above mentioned. If carbonated potash was used to precipitate the oxyd, some crystals of this salt also are formed.

Vauquelin relates that the Paris jewellers were ignorant of the fact that alkalies will not precipitate the whole of the gold from its solution, and therefore were in the habit of incurring a very great loss of this precious metal by taking no care of the washings when this mode of employing gold was used.

*Oxyd of Gold.* Mr. Oberkampf endeavoured to ascertain the proportions of the dark brown oxyd separated by potash from the muriatic solution, by enclosing a portion of it, still wet, in a bent glass tube closed at one end, heating it till the whole was reduced, and estimating all the products. The oxyd was not dried, to avoid the partial reduction that takes place, and it was totally soluble in muriatic acid, and therefore unmixed with any reguline gold. The results of three experiments gave 100. of metal with 9.82, with 10.21, and 10.6 oxygen. The mean of the three is 10.01 oxygen, which would make 100 parts of the oxyd to consist of 90.9 gold, and 9.1

oxygen, but the difference between the highest and lowest estimation being nearly a tenth, this can only be considered as a tolerable approximation to accuracy.

It is highly probable that this is the *peroxyd* of gold, and if there is any lower state of oxygenation it must be looked for in the purple powder to which gold is reduced by combustion, either by means of a powerful electric or galvanic apparatus, as described in our former article.

Professor Berzelius, whose authority must always carry much weight, has given a somewhat different view of the oxydation of gold, but at present we only have a short extract of his experiments.<sup>e</sup> He observes that the muriat of gold has two degrees of saturation. With excess of acid it forms yellow needled crystals, and the base of this is the peroxyd of 12.077 oxygen to 100 of metal. When this is perfectly neutral it is of a deep orange colour. If this latter salt is heated till it no longer gives out oxymuriatic gas, a saline mass insoluble in water is left, which is a muriated *suboxyd* of gold, and when decomposed by potash gives a green suboxyd containing only 4.026 of oxygen to 100. of metal. This suboxyd however exists but a few moments as such, being speedily reduced to metallic gold and peroxyd. As this proportion of oxygen is only a third of that of the suboxyd, the author conjectures that an intermediate definite oxyd must exist, which possibly may be the purple powder of Cassius, or the purple oxyd formed on many occasions with the salts of gold and animal or vegetable matters. As no particulars of the experiments are given, we are unable to state the many difficulties which immediately occur with regard to these positions.

*Purple precipitate of Cassius.* The mode of preparing this very singular compound has been amply described in our original article, but we shall add some very ingenious conjectures of Proust on the nature of this compound. It is prepared, as is well known, either by adding a solution of muriated suboxyd of tin to the muriat of gold, or by immersing in the solution of gold some pieces of metallic tin. When this powder is digested in nitro-muriatic acid, it loses its colour, gives a yellow solution of gold, and leaves a heavy sandy transparent peroxyd of tin. Muriatic acid assisted by heat has the same effect. Hence one of the component parts of this powder is peroxyd of tin. The other is gold, but it has been doubted

<sup>e</sup> Ann Chim. tom. 83. p. 166, being an extract from a memoir given to the Stockholm Academy.

whether, besides metallic gold, any portion of it is in the state of oxyd. That the oxyds of tin and gold are united by some kind of affinity, and not merely mechanically mixed seems proved by the following facts: the purple powder is perfectly soluble in liquid ammonia, forming a vivid purple liquor; but the metallic precipitates of gold are not so soluble in ammonia, and the oxyd of tin is but imperfectly so: also mercury, which so readily takes gold from most other combinations, has no effect on the purple powder though shaken with it. A hundred grains of the purple powder digested with weak aqua regia, gave, by Proust's experiments, a solution of gold, from which sulphat of iron separated 24 grains of metallic gold. The remaining peroxyd of tin weighed 70 grains, and hence 6 grains of the peroxyd must have been dissolved in the acid along with the gold. Therefore the gold in this preparation unites with about three times its weight of oxyd of tin. By the experiments of Duportal it appears that the degree of dilution

much influences the quantity of this precipitate, so that when a very weak solution of gold and of muriat of tin are employed, one part of gold will produce as much as  $5\frac{1}{2}$  parts of the purple precipitate.

The sulphated suboxyd of tin will also produce the purple precipitate with the solution of gold.

#### GREEN-EARTH.

There have been two recent analyses of this substance, one by Klaproth and the other by Vauquelin, the results of which are as follows.

K.	V.	
53.	—	52. silex
2.	—	6. magnesia
28.	—	23. oxide of iron
10.	—	7.5 potash
0.	—	7. alumine
6.	—	4. water
<hr/>		
99.	—	99.5
<hr/>		

## II

**HARMOTOME.** Kreuzstein, W. Cross stone, Jam.

The colour of this mineral is white, semi-transparent, with a shining lustre between vitreous and pearly. It occurs only crystallized, in broad tetrahedrons with rhombic pyramidal terminations, hence the entire crystal may be considered as a dodecahedron. The crystals are either single or cruciformly aggregated, intersecting each other at right angles, so that the axes of the two crystals coincide. Its hardness is somewhat superior to that of glass: its fracture at right angles to the axis of the crystal is uneven and small conchoidal, in other directions it is foliated. Sp. gr. 2.3. Becomes phosphorescent by heat, giving out a greenish yellow light. Intumesces before the blowpipe.

The cruciform variety has been analysed by Klaproth, and the single crystals by Tassaert, with the following results.

K.	T.	
49.	—	47.5 Silex
18.	—	16. Barytes
16.	—	19.5 Alumine
15.	—	13.5 Water
<hr/>		
98.	—	96.5
<hr/>		

The cruciform variety occurs in mineral veins

at Andreasberg in the Hartz, and at Strontian in Argyleshire; the single octohedrons have only been observed lining agate balls at Oberstein.

The only mineral likely to be mistaken for Harmotome is Jargoon in small dodecahedral crystals; the latter however is infusible before the blowpipe and possesses a specific gravity nearly twice as great as the former.

**HYALITE.** Muller glas.

This substance bears a perfect resemblance in its external appearance to gum Arabic. Its colour is greyish white or yellow, between translucent and transparent, with a vitreous lustre. It is harder than glass, breaks easily and with a flat conchoidal fracture. It occurs lining cavities and forming irregular botryoidal concretions in Wakke at Frankfort on the Mayn. It appears to be nearly allied to semi-opal.

**HYDRARGILLITE.** See WAVELLITE.

**HYDROSULPHURET.** See SULPHURETTED HYDROGEN.

**HYPERSTENE.**

The mineral designated by this name in the Tableau Comparatif of Haüy is the Labrador HORNBLÉNDE of the German and English mineralogists. Its external characters will be found on referring to the article Hornblende in the Dictionary; the crystallographical characters

which have induced M. Haüy to form of it a separate species are the following.

Primitive form, a rhomboidal prism the alternate angles of which are  $100^\circ$  and  $80^\circ$ ; with distinct joints in the direction of the short diagonal, and with others less distinct in the direction of the long diagonal. Sp. gr. 3.4. Its component ingredients, according to Klaproth, are

54.25	Silex
14.	Magnesia
2.25	Alumine
1.5	Lime
24.5	Oxyde of iron
1.	Water
<hr/>	
97.50	
<hr/>	

## I J

ICHTHYOPHTHALMITE. Fischaugenstein, W. Apophyllite, H.

The colour of this mineral is very pale yellowish, redish or greenish, more or less transparent, and with a shining pearly lustre. It occurs massive, with a foliated structure, or crystallized in rectangular parallelipeds approaching to the form of a cube or of a table, in the latter case the edges are irregularly bevelled and more or fewer of the solid angles are replaced. The cross-fracture is fine-grained uneven, the longitudinal is perfectly foliated. It has natural joints in three directions at right angles to each other, but of these only one is visible without the assistance of a strong light. Its hardness is a little superior to that of fluor spar, and it is very easily frangible. Sp. gr. 2.46.

When exposed to the flame of a candle it exfoliates; before the blowpipe it is fusible with difficulty into a white enamel; by digestion in cold nitric acid it breaks down forming a kind of jelly. It has been analyzed by Vauquelin and Rose with the following results.

V.	R.
51.	— 55. Silex
28.	— 25. Lime
4.	— 2.25 Potash
17.	— 15. Water
<hr/>	
100.	97.25

It occurs at Hellesta in Sweden.

IOLITE. Dichroite H.

The colour of this mineral, when viewed by transmitted light in a direction parallel to the axis of the crystal, is an intense Prussian blue, and when viewed in the opposite direction is brownish yellow. It occurs in irregular aggregated grains, or crystallized in regular hexahedral prisms (its primitive form) or in dodecahedrons. Its hardness is a little greater than that of quartz; and it breaks easily, with a shining conchoidal fracture, passing into imperfectly lamellar. The crystals are usually translucent, the grains opaque. Sp. gr. 2.56.

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It melts with difficulty before the blowpipe into a very pale greenish grey enamel. It has not as yet been analyzed.

It has been found only at Cape de Gattes, imbedded in a peculiar kind of conglomerate.

IODINE.—See the addendum to this appendix.

IRON. § 1. Ores of.

An interesting examination of the brown and ochreous ores of iron has been published by M. Daubuisson (Jour. des Mines. xxviii. p. 443), from which it appears that these ores, which by mineralogical writers have been divided into several species wholly unconnected with each other, are in fact so closely related as to constitute a single species. The essential component ingredients of all the varieties of this species are, per-oxyd of iron and water, in the proportion of about 85 of the former to 15 of the latter. When scraped or pulverized they are of a brownish-yellow colour, which changes to red or redish-black by calcination. They contain casual and variable proportions, but upon the whole very small, of oxyd of manganese, carbonate and phosphate of iron, and silex and alumine.

The name given to this species is *Hydrate of Iron*, it being the only one of the ores of this metal into which water enters as a constituent part. Its varieties are the following.

Var. 1. Brown Hæmatite.

External form botryoidal or mammillated; colour chesnut-brown; texture fibrous; yields to the knife; sp. gr. 3.6—4.0.

Composed of 79. to 82. Peroxyd of Iron  
15. — 14. Water  
2. — 2. Oxyd of Manganese  
3. — 1. Silex

99. — 99.

Var. 2. Compact brown ironstone.

Amorphous; colour dark brown; fracture compact and even, often presenting small cavities; rather harder than var. 1. Sp. gr. 3.7.

P

Composed of	84. to 69. Peroxyd of Iron
	11. — 13. Water
	1. — 3. Oxyd of Manganese
	2. — 10. Silex
	0. — 3. Alumine
	-----
	98. — 98.
	-----

Var. 3. *Ætites*.

In concentric lamellar concretions from an inch to a foot or more in diameter; the external laminæ compact and moderately hard, but becoming softer as they approach the nucleus, which latter is often friable or loose ochre.

Composed of	76. to 78. Peroxyd of Iron
	14. — 13. Water
	2. — 0. Oxyd of Manganese
	5. — 7. Silex
	0. — 1. Alumine
	-----
	97. — 99.
	-----

Var. 4. *Pea ore*.

In grains or globular concentric concretions; yields to the knife. Sp. gr. 3.4.

Composed of	70. to 73. Peroxyd of Iron
	15. — 14. Water
	0. — 1. Oxyd of Manganese
	6. — 9. Silex
	7. — 0. Alumine
	-----
	98. — 97.
	-----

Var. 5. *Ochre*

Amorphous; colour yellowish brown; fracture earthy, soft or friable.

Composed of	83. Peroxyd of Iron
	12. Water
	5. Silex
	-----
	100.
	-----

Var. 6. *Bog ore*.

Amorphous, more or less cellular, the cells often lined with blue phosphate of iron; colour blackish brown; fracture uneven, passing into flat conchoidal; lustre resinous.

Composed of	61. Peroxyd of Iron
	19. Water
	7. Oxyd of Manganese
	6. Silex
	2. Alumine
	2.5 Phosphoric acid
	-----
	97.5
	-----

That variety of iron pyrites, usually called the radiated, has of late been formed by Haüy into a distinct species, by the name of "Fer sulphuré blanc,"<sup>a</sup> *White Pyrites*.

Its general colour is considerably lighter than that of the common pyrites, being, when fresh and undecomposed, a perfect tin white, passing by decomposition into brass yellow and steel grey. Its primitive form is a rhomboidal prism, the alternate angles of which are 106°. 36' and 73°. 24'; its usual form however is the octohedron variously modified. It occurs in small crystals, but more usually in various particular shapes, such as reniform, stalactitic, &c. It gives fire with steel. Sp. gr. 4.75.

Before the blowpipe it gives out a light vapour with a sulphureous odour, and is afterwards attracted by the magnet; characters that distinguish it from arsenical pyrites, to which in colour and crystalline form it bears a great resemblance. It decomposes much easier than common pyrites into sulphate of iron.

§ 2. *Analysis of Iron and its Ores.*

Some important recent discoveries on this head deserve here to be mentioned.

Separation of Iron and Manganese.

Various methods of separating the mixed oxyds of these two metals have already been detailed in the articles IRON and MANGANESE, of the Dictionary: to these however may still be added the two following. It has been found by Berzelius and Hisinger,<sup>b</sup> that benzoate of ammonia is equally efficacious with succinate of ammonia in separating iron from manganese. Benzoate of ammonia is prepared by neutralizing liquid ammonia with pure sublimed benzoic acid, and afterwards evaporating the liquor; during this last process, the salt will become acidulous, and in this state it is to be used, with the following precautions. The solution containing the mixed oxyds (the iron being in the state of peroxyd), is to be very accurately neutralized with ammonia, and to be considerably diluted; the benzoate is then to be added drop by drop, as long as any precipitate falls down; the whole being now thrown on the filter, a bulky pale redish-yellow mass is obtained: this, after repeatededulcoration with cold water (for in hot water it is more or less soluble) is to be dried at the temperature of boiling water, and is then pure benzoate of iron, containing 25 per cent. of red oxyd. If it is an object to save the benzoic acid, the metallic salt may be digested in liquid ammonia for some hours, by which it will be entirely decomposed; the alkaline

<sup>a</sup> Journ. des Mines xxx, p. 241.

<sup>b</sup> Stockholm Trans. or Phil. Mag. for 1812.

benzoate being contained in the solution, and the red oxyd of iron subsiding to the bottom of the vessel.

The method at present relied on by Vauquelin,<sup>c</sup> as the most simple, and at the same time the most exact, is to digest the mixed oxyds in sulphuric acid, to evaporate the mass to dryness, and then to calcine it at a low heat, in order to decompose the sulphate of iron; the residue being now carefully washed with warm water, the whole of the sulphate of manganese in a state of perfect purity is taken up. From this solution the manganese is obtained in the state of oxyd, by means of carbonate of soda and subsequent calcination.

*Separation of Manganese and Magnesia.*

This is another of the practical difficulties in the analysis of the ores of iron. One way of effecting the separation of these substances is the following.

Having by means of caustic fixed alkali got rid of the silex and alumine, the residue insoluble in that menstruum is to be dissolved in sulphuric acid, and largely diluted; to this is to be added a solution of super-carbonated potash as long as any precipitate is formed. The precipitate consists of the metallic oxides, and the clear solution retains the lime and magnesia. This latter being then boiled, the sub-carbonates of the earths are deposited, and may be separated by the usual methods: their purity from iron or manganese is evinced by their retaining a white colour after calcination. Another method, recommended by Vauquelin, is to dissolve the mixed carbonates of manganese and of magnesia in acetic acid, and then to add hydrosulphuret of ammonia, which throws down the manganese, but has no such effect on the magnesia.

Hisinger's method is to calcine the mixed carbonates in order to separate the carbonic acid, to treat the residue by dilute sulphuric acid, which will dissolve the whole of the magnesia, and only part of the manganese; and then to add to the solution prussiate of potash, which will leave all the magnesia in the liquor, and separate only the manganese; after which the magnesia may be recovered by caustic potash.

It appears from a recent examination by Vauquelin,<sup>d</sup> of certain bog-iron-ores, that besides the usual earths and iron and manganese, they contain phosphoric acid and oxyd of chrome. Thus the analysis is complicated by the addition of two more substances, and the practical difficulties of separating accurately all the ingre-

dients, are such as appear almost to have eluded the skill and resources of this truly eminent chemist. The following were the processes employed by him in the resolution of this problem.

The ore, previously pulverized, was fused with caustic potash and then digested in water, to which it communicated an intensely green colour. The portion insoluble in water was a second time treated with potash, and again digested in water. The two aqueous or rather alkaline solutions were added together and boiled, the green colour disappeared, and a brown precipitate was obtained, consisting of oxyd of manganese mixed with a little silex and oxyd of iron.

The solution, after separation of the manganese, was of a pale yellow colour indicating the presence of chrome; accordingly it was saturated with nitric acid, and a solution of nitrate of mercury made in the cold, was dropped in; a white precipitate was thus obtained, which on examination proved to be phosphate of mercury. The yellow colour of the solution having disappeared, and containing, on examination, an excess of acid, a few drops of caustic potash were added, which threw down a brownish red precipitate, consisting of chromate of mercury with a little phosphate. Into the solution, which was still acid, was dropped a little nitrate of silver, and immediately an orange coloured precipitate subsided, which did not give a green colour with borax, and was phosphate of silver. Potash was again added to the liquor, and occasioned a very voluminous lemon-yellow flocculent precipitate, which by drying acquired a green colour, and on examination proved to be chromate of mercury, containing silver and a little alumine and silex.

A somewhat different method was followed by the same chemist in his examination of the scoriae produced in the fusion of the ore, which was the subject of the preceding analysis. The scoria was twice fused with an equal weight of caustic potash, and the portion thus rendered soluble in water, afforded a deep green solution, from which by boiling, the manganese was separated in the form of a brown oxyd. To the solution was now added nitrate of ammonia, which threw down a mixture of silex and alumine. The residual liquor was now slightly supersaturated with nitric acid, and boiled for a quarter of an hour, in order to separate entirely the carbonic acid. Lime water was then added, and a very pale yellow precipitate was deposited, which became green in drying, and on exami-

\* Journ. des Mines xxvii. 498.

Journ. des Mines xx. p 382.

nation proved to be phosphate of lime, with a little chromate. Fresh nitrate of mercury was now poured in, and a brownish yellow precipitate fell down, which proved to be chromate of mercury with excess of base.

§ 3. *Reduction of Ores.*

One of the most important and successful enquiries on this head is the controversy that has arisen in France relative to the analysis and the general treatment of spathose iron; an ore which does not occur in this country in sufficient abundance to be made use of, but from which the celebrated irons of Styria and of the Tyrol, as well as those of various parts in the South of France, are entirely procured. The principal papers relative to this controversy, are contained in the *Annales de Chimie*, vols. lvi. lvii. lviii. lxii, and in the *Journal des Mines*, vol. xix. From these it appears that besides the carbonate of iron, which composes by far the greatest proportion of the ore in question, there is contained in it magnesia, varying in quantity from the smallest perceptible portion to nearly 14 per cent.; also the carbonates of manganese and of lime. The superintendents of the iron forges, where this kind of ore is manufactured, led by experience independently of any theory, have long been in the habit of sorting it into fusible and refractory ore. Of these the former may be made use of fresh from the mine, whereas the other is in its recent state excessively refractory, and requires exposure to the air for a space of from one to twenty years before it can be advantageously employed.

M. Descotils, who appears to have prosecuted this interesting enquiry with the most success, conceived that the difference between the two varieties, was principally, if not entirely owing to the magnesia. For this purpose he selected two varieties, one of which contained a considerable and the other only a very minute proportion of magnesia: from each of these he detached a portion, and subjected both to an assay at the same time, and in the same furnace. The former afforded a mass of minute metallic grains, which had not run together in consequence of the non-vitrification of the scoria; the latter on the contrary gave a perfectly formed and well melted button of metal. The result however was not quite conclusive, because this last variety contained a considerable quantity of manganese, to which its fusibility might be ascribed, another portion therefore of the same ore was freed from its manganese, and being submitted to the assay, yielded as perfect a but-

ton as the other; the only difference between them being that the former afforded a white and the latter a grey metal.

In a subsequent memoir on the same subject, M. Descotils pursues his researches into the power of magnesia to render refractory the most fusible ores of iron. A portion of the iron ore of Elba was submitted without any flux to a strong heat, and afforded a perfect button, while 100 parts of the same specimen, to which 15 parts of magnesia had been added, gave a precisely similar result to the assay of magnesian spathose iron. He also examined a specimen of refractory spathose iron, and found it to contain 4 per cent. of magnesia, and on comparing it with specimens of the same ore that had become fusible by exposure to the air, he found that this latter was almost wholly free from magnesia. Hence it appears that the material change operated on the refractory spathose iron ores by exposure to the air, either with or without a previous roasting, is the separation of the magnesia. With regard to the mode by which this separation is effected, it is obvious that where the ore contains pyrites, the decomposition of this will furnish sulphate of iron, which coming in contact with the carbonated magnesia, will be again decomposed, and the sulphate of magnesia hence resulting, will be washed away by the rain. In confirmation of this it was found that the washings of a heap of refractory ore that had been exposed for a long time to the air, actually afforded sulphate of magnesia with a little sulphate of lime. In those cases where the ore contains little or no pyrites, the magnesia appears to be rendered soluble by the excess of carbonic acid, which is continually escaping from the iron as it becomes more oxygenated.

§ 4. *Physical properties of Iron.*

In addition to those properties already mentioned in the Dictionary, it may be stated as a recent discovery, and one likely to be productive of much practical utility, that cast iron when heated yields readily to the saw.<sup>c</sup>

The precautions required in this operation are, that the piece of iron should be heated equally, for which purpose a reverberatory furnace is much better than a forge fire: That the temperature should be as high as the iron can bear without becoming pasty, in which latter case the teeth of the saw are obstructed, and the work proceeds slowly: That two saws should be made use of if the piece to be cut is of any considerable thickness, working with the first till it grows hot, and then employing the second

<sup>c</sup> *Ann. de Chim.* lxxii. p. 218.



while an assistant is cooling the first in water and drying it: That the saw should be worked rapidly, steadily, and at full length. These precautions being duly observed, cast iron may be cut by a common saw with the same ease as dry box-wood, and without injury to the tool.

§ 5. *Chemical properties of Iron.*

In the articles *Sulphuret and Affinity* in this Appendix, we have given some observations on the different sulphurets of iron, natural and artificial, in addition to the very full notice of the subject in our original article *Iron*. We shall only here relate the particulars of Berzelius's experiments on this subject, as they appear to have been undertaken with great care.<sup>f</sup>

*Subsulphuret of Iron.* One part of very fine sheet iron almost entirely free from carbon, mixed with three parts of pure sulphur, was slowly heated to redness in a glass retort with a luted receiver. The iron when cold retained its form, but was covered with greenish shining scales which readily peeled off. These scales were the subsulphuret of iron, which was still magnetical when pulverized. Two parts of these scales digested in nitro-muriatic acid, till dissolved, gave with muriated barytes 5.38 parts of sulphat of barytes. Estimating the acid of 100 parts of this sulphat at 34, and the sulphur of this 34 at 13.797, the 5.38 give 0.742 of sulphur (or 37.1 per cent.) in the subsulphuret. The supernatant liquor gave with ammonia 1.82 of peroxyd of iron, equal to 1.26 of metallic iron, and  $1.26 + 0.742 = 2.002$ , so that there is an excess of .002 over the sulphuret analyzed.

The composition of this subsulphuret of iron may therefore be taken at

Sulphur	37.	—	58.75
Iron	63.	—	100.00
	100		158.75

*Supersulphuret of Iron.* The purest crystallized iron pyrites was taken as the best specimen of this compound. It was examined by being first roasted on a platina plate, under a muffle, till all the sulphur was expelled, and the iron converted to red oxyd. Deducting the proportion of metallic iron in the sulphuret from that of the red oxyd, and estimating the rest of the pyrites as sulphur, (abstracting a small proportion of silex which remained after dissolving the red oxyd in muriatic acid) the composition of the pure supersulphuret of iron will give almost exactly a double portion of sulphur to

that in the subsulphuret, being actually found to consist of

Sulphur	53.92	—	117
Iron	46.08	—	100
	100.00		217

If the sulphur were 117.5 to 100 of iron the proportion would be exactly double that of the subsulphuret.

Though these proportions are very well defined, it appears that there may be several intermediate degrees of sulphuration of iron when prepared artificially, which may be partly owing to a mere solution of iron in sulphuret of iron, that may probably take place to an indefinite extent, and independent of true chemical combination.

*Iron and Oxygen.* Few parts of analytical chemistry have been so much attended to as the different degrees of oxygenation of iron, but the discordance between the results of several chemists (which is not trifling considering the pains taken) shews the difficulty of the subject. Berzelius has shewn in a very satisfactory manner that in most kinds of iron a new element must be taken into account, namely, *Silicium*, which is obtained from the siliceous part of the flux employed in the reduction of iron ores, and alloys the iron. See the article *SILICIUM in this Appendix*. The same eminent chemist has also shewn the difficulty (hitherto almost insuperable) of ascertaining the carbon in all manufactured iron with absolute accuracy, owing to the conversion of a portion of it into a volatile black oily matter which mixes with the hydrogen gas obtained during the solution of iron. Therefore whenever a given portion of the purest iron is converted into oxyd, to ascertain the elements of this oxyd a certain allowance must be made for the carbon which always is present, and for the silicium which is generally present, and appears in the form of silex after the action of acids.

The peroxyd or red oxyd of iron is the only one in whose composition the results of various chemists agree with tolerable accuracy, though even in this there is too much discordancy.

The peroxyd is thus composed, according to Berzelius' average results, on an analysis in which the carbon and silex are attended to.

Iron	69.34	—	100.00
Oxygen	30.66	—	44.25
	100.00		144.25

<sup>f</sup> An. Chem. tom. 78.

*Suboxyd of Iron and Black Oxyd.* It has been advanced by Proust, and pretty generally allowed, that there are only two oxyds of iron, viz. the red and the black. The red is the peroxyd just described, and is without question the highest known state of oxygenation of this metal. It is equally certain that a definite oxyd of inferior degree exists, to which the name of black oxyd may be given; but there is a good deal of reason to conjecture the existence of a third oxyd, still lower in its proportion of oxygen, to which therefore the term *Suboxyd* is more properly applicable. Thenard has attempted to establish the existence of this oxyd, and we shall also find that the hypothesis of definite proportions (explained in the article *Affinity* in this Appendix) renders this still more probable, as it will correspond to an oxyd consisting of an atom of iron to an atom of oxygen, the black oxyd being two atoms of oxygen to one of iron, and the red oxyd three atoms of oxygen to one of iron. We shall however drop the consideration of this lowest oxyd, and only mention the *Black Oxyd*, *Suboxyd*, or *Oxidulum of Iron*, as commonly received.

This black oxyd is the base of the *Green Sulphat of Iron*, and its elements have been estimated by Buckholz, at 23 oxygen in 100 of oxyd, or 29.88 oxygen on 100 of metal. Berzelius analyzed this in the following way: some green sulphat of iron was made by dissolving sulphuret of iron in dilute sulphuric acid, crystallizing the salt and washing it with alcohol, to separate the adhering liquor, and drying it in a moderate warmth on blotting paper. Ten parts of this crystallized salt were heated by themselves in a retort, in a heat below redness, by which 4.63 parts of water were expelled. The heat was then raised to redness, till all the sulphuric acid was driven off, during which the oxyd passed to the state of red oxyd, which weighed 2.82, equal to 1.95 metallic iron. The sulphuric acid in 10 parts of this salt had been found by a previous experiment with a barytic salt, to amount to 2.842, so that the acid, the iron, and the water together, amounted to 9.422, leaving 0.578 for the oxygen combined with the iron; which gives an oxydation of 29.6 oxygen to 100. of iron, or very nearly the same as that given by Richter. As 29.5 of oxygen will exactly accord with a definite proportion, this number may be assumed without much error, and therefore the black oxyd of iron will consist of

Iron	77.22	—	100.00
Oxygen	22.78	—	29.5
	100.00		129.5

Therefore the oxygen of the black oxyd is to that of the red oxyd as  $1:1\frac{1}{2}$  to a given quantity of iron; for  $29.5 \times 1\frac{1}{2} = 44.25$ .

If a lower degree of oxydation of iron is found, it may be expected to be in the proportion of 14.75 of oxygen to 100. of iron, and then the black oxyd will contain two proportions of oxygen, or  $14.75 \times 2 = 29.5$ , and the red oxyd, three proportions, or  $14.75 \times 3 = 44.25$ .

But M. Gay Lussac is stated to have lately given a memoir on the subject of the oxyds of iron, in which, as we learn from a short extract, he shews the existence of three distinct oxyds, but instead of finding a lower degree than that of the black oxyd just described, he states an intermediate oxyd between this and the red oxyd. As we have not the particulars of the experiments, we shall only mention that the three oxyds have respectively to 100. of iron 28.3, 37.8, and 42.31 of oxygen. The lowest of these, which he terms *white oxyd*, he states to be obtained when iron decomposes water by the assistance of acids, but without the acid itself being changed, as when iron is dissolved in dilute sulphuric or muriatic acid. It is the base of the green sulphat of iron. The solutions of this oxyd are precipitated white by fixed alkalies, and by prussiat of potash; ammonia dissolves it copiously. The next oxyd, or that of 37.8 oxygen, is produced when iron is burnt in oxygen gas, or when water alone is decomposed over red hot iron. It is called here the *black oxyd*. This oxyd is separated of a deep brown by alkalies, or of a green, when much diluted. It is very magnetical, gives blue precipitates with the prussiat, and a black with galls, is soluble in ammonia though less than the last mentioned oxyd, and also in the supercarbonated alkalies. The next oxyd is the saturated or *red oxyd* of 42.31 oxygen, universally known, and is best obtained by passing vapours of nitric acid over iron. When the middle of these three oxyds (or black oxyd according to the author) is dissolved in sulphuric acid, and the solution crystallizes, the crystals are the green sulphat, the base of which is the white oxyd, and red sulphat remains in solution, so that the oxygen of the black oxyd divides unequally, and both a higher and lower oxyd are produced.

The particulars of this memoir will doubtless be highly interesting. We may observe that these numbers expressing the degrees of oxydation, do not very much deviate from a proportion in which the common divisor is 7.07, in which case the white oxyd would contain 4 proportions (28.28), the black oxyd 5 proportions (35.35), and the red oxyd 6 proportions (42.42). At all events the concurring experiments of all later enquirers seem to prove at least two oxyds of iron, one of which consists of about 28. oxygen to 100 of metal, and the other (which is the red or peroxyd) contains  $1\frac{1}{2}$  this proportion, or about 42 oxygen to 100 of metal.

BND OF APPENDIX TO VOL. I.

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## APPENDIX TO VOL. II.

### L

LACTIC ACID. See BLOOD.

LACTIALITE. Haiiyne.

The colour of this mineral in those specimens that are opaque is indigo blue, and in those which are translucent is bluish green. It occurs massive, in grains, and in a single instance in extremely minute brilliant crystals. Its hardness is a little superior to that of quartz; it is very brittle; its fracture is vitreous, uneven; sp. gr. about 3.2.

Before the blowpipe it is infusible *per se*, but with borax affords a yellow glass. When finely pulverized it gelatinizes with the mineral acids. Its constituent parts, according to Vauquelin, are,

- 30. Silice
  - 15. Alumine
  - 20.5 Sulphat of lime
  - 11. Potash
  - 1. Oxide of iron
  - 5. Lime
- an atom of sulphuretted hydrogen

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82.5

17.5 loss, probably for the most part water.

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100.0

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It occurs at the lake Nemi, and near Albano and Frascati, accompanied by mica and green hornblende; and at Monte Somma among the ejections of Vesuvius, accompanied by idocrase, augite, mica, and meionite.

In many of its external characters and in its chemical composition, this mineral bears a striking analogy with lapis lazuli.

LAUMONITE.<sup>a</sup> EFFLORESCENT ZEOLITE.

This mineral occurs in aggregate crystalline masses, deeply striated externally, or in separate crystals. Its primitive form is a rhomboidal prism, the angles of which approach to right angles: this figure is further divisible by joints parallel to its axis and to the greater diagonal of the terminal planes. Its fracture is

lamellar; it is colourless and transparent. Sp. gr. 2.23.

When exposed to the air it undergoes with more or less rapidity a spontaneous change, in consequence of which it first loses its transparency, and presents a shining white appearance, then the natural joints, especially those parallel to the axis of the prism, become very apparent, and lastly the whole separates into a white powder similar to that resulting from the decomposition of Glauber's salt. This change can only be prevented by immersion in water or by a varnish.

The laumonite was at first supposed to be peculiar to the lead mine of Huelgoet in Brittany, but M. de Bournon has since discovered it among specimens from Ferroe, from near Paisley, and from Portrush in Ireland; none of these however are so strikingly efflorescent as the specimens from Brittany.

LEAD.

§ I. Ores of.

Native Minium.<sup>b</sup> — Plomb oxydé rouge *Hauy*.

The colour of this substance, like that of factitious minium, is a vivid scarlet: it is amorphous and pulverulent, but when examined with a lens exhibits a flaky and crystalline texture. When gently heated before the blowpipe it acquires a darker colour, but recovers its original tint by cooling; by a stronger heat it melts to litharge, and on charcoal is reduced to metallic lead. It occurs in the lead mines of Breylau in Westphalia, sparingly disseminated through compact calamine, and mixed with galena and carbonate of lead.

*Arseniate of Lead.*<sup>c</sup>

The following particulars concerning this ore (recently discovered in Cornwall by Mr. Gregor) may serve to correct the account given in the Dictionary.

Its colour is wine yellow passing into brownish yellow; it occurs in small slender hexahedral crystals and capillary fibres: it varies from

<sup>a</sup> Geol. Trans. i. p. 77.

<sup>b</sup> Phil. Trans. for 1806. p. 267.

<sup>c</sup> Ibid. 1809. p. 195.

translucent to transparent with a vitreous resinous or silky lustre: when transparent it scratches glass; it is easily frangible, sp. gr. 6.4.

Before the blowpipe it melts into a brownish yellow mass; when ignited on charcoal it exhales arsenical vapours, and is reduced to metallic lead. It appears to be composed of

69.76	Oxide of lead
26.4	Arsenic acid
1.58	Muriatic acid

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97.74

2.26 silex, alumine, oxide of iron  
and loss

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100.00

It occurs in Huel Unity, in the parish of Gwennap, Cornwall, mixed with native copper, grey and black copper, and octohedral red copper.

§. 2. *Chemical Properties.*

It is generally admitted that there are three oxyds of lead, the *yellow*, the *red*, and the *brown*, or puce-coloured. Of these, the yellow is the lowest in oxydation, but its elements have been very differently stated by chemists. It is the most important of all in a chemical view, as it appears to be the basis of most of the salts of this metal.

The oxydation of lead was thus examined by professor Berzelius.<sup>d</sup>

*Yellow Oxyd and Litharge.* 10 parts of pure lead (reduced from the crystallized nitrat) were dissolved in nitric acid in a glass vessel, the solution evaporated to dryness in a platina vessel, and made red-hot. It left 10.77 parts of yellow oxyd. A second experiment gave 10.775 parts. A third experiment made entirely in a glass vessel, gave 10.78. It was found that a minute quantity of the nitrat of lead had sublimed in the experiment, which of course made this result of yellow oxyd rather too little. 10 parts of lead dissolved in nitric acid were precipitated by carbonat of ammonia, giving 12.9025 parts of carbonat of lead, which left 10.75 of yellow oxyd when ignited. Another similar experiment gave 10.95. Therefore, making a little allowance for loss, the yellow oxyd is thus composed.

Lead . . . 92.765	100.0
Oxygen . . . 7.235	7.8

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100.000      107.8

*Red Oxyd or Minium.* Common red lead contains besides the proper red oxyd, some

yellow oxyd, sulphat and muriat of lead, oxyd of copper, and silver. The yellow oxyd was dissolved out by weak distilled vinegar which hardly acts upon minium. The minium thus purified was strongly heated, by which it was changed to yellow oxyd by losing oxygen, and the other impurities being allowed for, it appeared that purified minium consisted of

Lead . . . 90	— 100.
Oxygen . . . 10	— 11.07

---

100 — 111.07

*Brown Oxyd.* This oxyd is produced as mentioned in our original article, by digesting nitric acid on minium, which deoxygenates a part and superoxygenates the remainder, the former being reduced to yellow oxyd and dissolved in the acid, and the latter being the brown oxyd. This is composed, according to Berzelius, of

Lead . . . 86.51	— 100.0
Oxygen . . . 13.49	— 15.6

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100.00 — 115.6

Hence it appears probable, that in these three states of oxydation, 100 parts of lead take up oxygen in the proportion of 1, 1½ and 2, the numbers 7.8, 11.07 and 15.6 being nearly in this ratio.

*Sulphuret of Lead.* Equal parts of lead and pure sulphur were melted together in a retort, and kept at a red heat till nothing further was expelled. The composition of the sulphuret thus found, gave

Lead . . . 86.51	— 100
Sulphur . . . 13.49	— 15.6

---

100.00 — 115.6

Lead and sulphur appear to unite in no other proportions. When this sulphuret of lead is fully oxygenated by boiling with nitro-muriatic acid, the whole is exactly changed to neutral sulphat of lead, the sulphur when converted into sulphuric acid being just sufficient to saturate the lead when changed to yellow oxyd, (this oxyd being the base of all the salts of lead.) See the article *Affinity*.

*Muriat of Lead.* 5 parts of yellow oxyd of lead dissolved in muriatic acid, and the solution evaporated to dryness in the same vessel, gave 6.187 parts of fused muriat of lead. A small portion of the salt however was

volatilized during the process. Muriat of lead therefore consists of from 80.8 to 81. per cent. of oxyd of lead, and 19. to 19.2 of acid.

10. parts of fused muriat of lead were dissolved in nitric acid, and the solution decomposed by nitrat of silver. The supernatant liquor was separately evaporated to dryness, and the soluble salt then dissolved out by water, by which a little muriat of silver that had been dissolved in the excess of nitric acid was recovered and added to the other portion. The whole of the muriat of silver when fused weighed 10.32 parts, which contain according to Berzelius 1.9644 of muriatic acid:

Another 10 parts of fused muriat of lead were dissolved in nitric acid, an excess of sulphuric acid added, the whole evaporated till all was driven off except sulphat of lead with a little sulphuric acid in excess; which last was separated by hot water. The neutral sulphat of lead well dried weighed 10.92, containing by estimation 8.03876 of suboxyd of lead. These two experiments very closely agree, so that fused muriat of lead may be taken as containing

Muriatic acid	. 19.644	— 100.00
Yellow oxyd of lead	80.356	— 409.06
	100.000	— 509.06

by one estimation, and by the other 19.61 per cent. of muriatic acid.

*Carbonat of Lead.* 10. parts of carbonat of lead dried at a high temperature were kept red-hot in a platina crucible, and left 8.35 of suboxyd of lead. The carbonat of lead therefore contains

Carbonic acid	. . . 16.5
Yellow oxyd of lead	83.5
	100.0

*Sulphat of Lead.* From a great variety of experiments, which agree pretty closely, professor Berzelius fixes the composition of this salt at

Sulphuric acid	. 26.346	100	35.9
Yellow oxyd of lead	73.654	279	100.0
	100.000	379	135.9

*Nitrat and Nitrite of Lead.* The salts produced by the combination of oxyd of lead and nitrous or nitric acid, are numerous and difficult to be made out with accuracy. Besides

the common crystallized nitrat of lead formed by the solution of lead in nitric acid, there are other compounds formed either by digesting nitrat of lead with an additional quantity of metallic lead (as mentioned by Proust) or with more oxyd of lead; or else by the partial decomposition of these salts, by which salts with excess of base are obtained.

In addition to what has been mentioned on this subject in our original article, we shall merely state the results of the experiments of Berzelius and of Chevreul.<sup>d</sup>

*Nitrat of Lead.* This well known salt which forms large white opaque octohedral crystals appears to contain no water of crystallization. It contains according to Berzelius

Nitric acid	. . . 32.7	— 100.
Yellow oxyd of lead	67.3	— 205.09
	100.	305.09

Chevreul agrees almost exactly with this calculation.

*Subnitrat of Lead.* This salt may be made in two ways, either by digesting the nitrat with oxyd of lead; or by adding ammonia to the nitrat, less than will decompose the whole salt, whereby a nitrat of ammonia and a subnitrat of lead are produced. Berzelius adopts the latter method. A precipitate took place on adding a little ammonia to nitrat of lead, which was welledulcorated and dried to separate all the ammoniacal salt. A portion of this gradually heated to redness in a retort gave out much uncondensable nitrous vapour and left 80.5 per cent. of bright lemon-yellow oxyd. It therefore contained no water but consisted merely of

Nitric acid	. . . 19.5	— 100.
Yellow oxyd of lead	80.5	— 412.9
	100.0	512.9

*Double Sub-nitrat of Lead.* The last experiment was repeated with the variation of digesting the mixed nitrat of lead and ammonia for some time and then washing the precipitate with boiling water. This precipitate dried and decomposed as before lost 9.7 per cent. of acid, and therefore consisted of

Nitric acid	. . . 9.7	— 100.00
Yellow oxyd of lead	90.3	— 930.92
	100.0	1030.92

M. Chevreul obtained the first subnitrat by

boiling the nitrat of lead with yellow oxyd and allowing the clear liquor to cool in a well corked phial (to keep out the carbonic acid of the atmosphere) by which a number of pearly crystalline scales separated, which form the subnitrat in question. This salt is sweet and astringent, and when a current of carbonic acid is passed through, much carbonat of lead separates, and the nitrat returns to the state of common nitrat. The elements of this subnitrat are stated at 19.86 per cent. of acid and 80.14 of yellow oxyd, which very closely agrees with Berzelius.

In the three nitrats of lead just described, 100 parts of nitric acid saturate 205.00, 412.9 and 930.92 parts of oxyd respectively. The two first are as nearly as can be expected in the simple ratio of 1:2, but the third does not coincide with any simple ratio. In all these the acid is the *nitric* and the oxyd is to all appearance the *yellow oxyd*.

*Nitrite of Lead.* This salt was first observed by Proust, and is obtained by boiling the common nitrat of lead with *Metallic Lead*, as described in our original article, and is considered by Proust as a nitrat of lead the base of which is at a lower state of oxygenation than the yellow oxyd, and by Dr. Thomson as a compound of the yellow oxyd with an *acid* at a lower state of oxygenation, and is therefore a *nitrite* of lead. It is obvious that either the acid or the oxyd must be in this state of diminished oxygenation, since in its preparation the metallic lead must absorb that portion of oxygen necessary for its solution from one or other or both of the constituents of the common nitrat of lead with which it is digested.

This subject has been examined with great care by Berzelius and Chevreul, with a remarkable agreement in their results.

When 20 parts of nitrat of lead are boiled in water with 12.4 parts of metallic lead (which is equal to the lead contained in the salt) the whole dissolves in some hours into a deep yellow liquid, which on cooling becomes the yellow crystallized mass described by Proust. This is the *Nitrite of Lead*. It has indeed a slight excess of base, so as to act like an alkali on vegetable colours, and therefore might with more strictness be called a *subnitrite*, but we shall retain the term of simple *nitrite of lead* to distinguish it from a subnitrite with a double proportion of base, to be presently described.

This nitrite of lead is also formed whatever be the proportion of lead employed with the nitrat of lead; but when the lead is in excess and the boiling too long continued, a brick-red salt

gradually appears, which is the proper *subnitrite of lead*.

The nitrite of lead forms yellow foliated crystals. Its taste is slightly astringent and sugary; 100 parts of boiling water dissolve about  $9\frac{1}{2}$  of the salt, but the same portion of cold water takes up scarcely more than  $1\frac{1}{4}$ . Sulphuric, nitrous and acetic acids decompose this salt and expel from it nitrous vapour, particularly when heated. Carbonic acid passed through a solution of this nitrite, partially decomposes it and separates a carbonated oxyd. Carbonated potash entirely decomposes it into carbonat of lead and nitrite of potash. When the nitrite is gradually heated it loses its acid and passes to the state of yellow oxyd.

The subnitrite of lead is produced, as above described, by boiling nitrat of lead for many hours with more metallic lead than it can take up: 10 parts of the nitrat by long boiling will thus dissolve about 12 parts of metallic lead, and the solution on cooling lets fall small brick-red crystalline plates, whilst the supernatant liquor contains a mixture of both these nitrites. These brick-red crystals are the *subnitrite of lead*, and consist of nitrous acid and a double portion of yellow oxyd of lead to that of the nitrite. This subnitrite is very little soluble in water, 3 parts requiring 100 of boiling water for solution. It is copiously precipitated by carbonic acid gas, or even by exposure to air. M. Chevreul gives the elements of the *Nitrite of Lead* to be

Nitrous acid	18.15	—	100.
Yellow oxyd	81.85	—	450.
	100.00		550.

and of the *Subnitrite of Lead*

Nitrous acid	9.9	—	100.
Yellow oxyd	90.1	—	910.
	100.0		1010.

Berzelius agrees pretty nearly with this estimation, so that the base of this subnitrite is a double proportion of that of the nitrite.

We shall conclude this article by noticing a singular production of the *Peroxyd* or *Brown oxyd* of lead observed by M. Chevreul. This oxyd is generally produced, as before mentioned, by digesting minium in nitric acid, by which a portion of it *loses* oxygen to pass to the state of yellow oxyd and dissolves in the acid, and the other part *gains* oxygen and becomes the insoluble brown oxyd. M. Chevreul has observed



this unequal partition of oxygen in a different way: some flint glass (containing much minium) was heated in a platina crucible with thrice its weight of caustic potash, and the fused mass was digested with water. An alkaline solution of silex and yellow oxyd of lead was produced, and on remaining at rest it deposited a brown crystallized powder, which was the brown oxyd, whilst the crucible itself and the platina spoon used to stir the materials were lined with a metallic coating consisting of an *alloy of lead and platina*. This singular fact can be explained by supposing that the alkaline solution at first contained the whole of the lead of the glass in the state of yellow oxyd, but that the affinity of

lead for platina then determined the precipitation of a small part of the lead in the metallic state on the platina of the vessel, whilst another portion of oxyd of lead taking up the oxygen of this reduced lead, passed into the state of brown oxyd, in which the metal is in the highest state of oxydation. That the brown oxyd was formed in consequence of the reduction of part of the oxyd of lead, and was not contained as such in the glass, is obvious from the intense heat employed in glass-making, which indeed is at all times sufficient to expell much oxygen, even from the minium used as a flux, and to reduce it to yellow oxyd.

LIME (*Basis of.*) See CALCIUM.

## M

### MADREPORITE.

A new analysis of this mineral has been published by Klaproth,<sup>a</sup> from which it appears to be composed of

93.	Carbonate of lime
0.5	Carbonate of magnesia
1.25	Carbonate of iron
0.5	Carbon
4.5	Siliceous sand

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99.75

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### MANGANESE.

An elaborate series of experiments on the salts and oxyds of this metal has been given by Dr. John of Berlin,<sup>b</sup> which appear to have been conducted with much attention. A few particulars may be mentioned.

*Regulus of Manganese.* This was prepared in the usual way, by reduction of the purified oxyd in a crucible lined with charcoal. The oxyd was prepared in the following manner. Some of the purest native black oxyd of manganese was dissolved to saturation in muriatic acid, a little nitric acid was added, the liquor was reduced by evaporation, then diluted with water, saturated with alkali and digested with pieces of iron to separate most of the copper contained in the solution. A little potash was then added, followed by oxalat of potash, which separated the iron in form of oxalat in twenty-four hours. The lead, if any, was then separated by sulphat of soda, and the manganese by carbonat of ammonia. But the carbonat of manganese is not yet quite free from copper, as prussiat of potash gives a peach-flower coloured

precipitate, instead of one perfectly white, which occurs when the manganese is quite pure. The carbonat of manganese must therefore be digested with water and pure ammonia, redissolved in sulphuric acid, and then just supersaturated with ammonia and digested for a time, by which the remaining oxyd of copper falls down mixed with a little oxyd of manganese, after which the supernatant liquor will yield with carbonat of ammonia a perfectly pure oxyd of manganese.

This purified oxyd was reduced in a Hessian crucible lined first with a paste of silex, alumine and charcoal, over which charcoal powder alone was pressed down and a conical cavity was cut out to receive the oxyd of manganese previously mixed with a little oil and repeatedly calcined, to produce an intimate union of the oxyd with the charcoal of the oil. The reduction was effected in a very intense heat of a forge-furnace, kept up for an hour and a half, after the crucible had been gradually heated for an hour. From 830 grains of the pure carbonat the author obtained repeatedly about 250 grains of the regulus of manganese.

This regulus when made from pure oxyd leaves about one per cent. of its weight of charcoal when digested with acids, but if it contains any iron, the charcoal is greater. This charcoal may be extracted by melting the metal again under borax, which requires less heat than that employed for the first reduction.

*Carbonat of Manganese.* All the solutions of manganese when decomposed by an alkaline carbonat give a white carbonat of manganese, which appears to be the only salt of this

<sup>a</sup> Analyt. Ess. ii. p. 218.

<sup>b</sup> Journ des Mines, tom. xxii. and xxiii.

species. The metal is in the state of suboxyd. When the carbonat is yellowish or brown it is probably (if no other metal is present) a mixture of carbonat and brown oxyd of manganese.

The white carbonat is tasteless, unchangeable by exposure to air in a low temperature, and may be dried in a gentle heat. When decomposed by ignition in close vessels it gives

Suboxyd of manganese	55.84
Water . . . . .	10.00
Carbonic acid . . . . .	34.16
	<hr/>
	100.0

The suboxyd left after ignition is greenish-grey, and this suboxyd may be considered as the basis of all the salts of manganese.

*Sulphat of Manganese.* Sulphuric acid when diluted dissolves metallic manganese with copious disengagement of hydrogen of a peculiar smell. 100 grains of metal are exactly saturated with 190 grains of sulphuric acid of 1.86 sp. gr. and this solution decomposed by carbonated ammonia gives 205 grains of carbonat of manganese dried at 77° Fahr. This will give 48.6 per cent. of metal in this carbonat.

Sulphuric acid dissolves the suboxyd of manganese with equal ease, and forms a solution exactly similar to the former, which crystallizes easily. This salt was analyzed by muriat of barytes to separate the sulphuric acid, and by carbonat of ammonia for the metallic oxyd. Estimating the acid of sulphat of barytes at 34 per cent. and the suboxyd of manganese at 55.84 per cent. of the dry carbonat, the crystallized sulphat of manganese contains

Sulphuric acid . . . . .	33.66
Suboxyd . . . . .	31.00
Remains for water . . . . .	35.34
	<hr/>
	100.00

*Muriat of Manganese.* The author has succeeded in obtaining large tabular crystals of this salt, quite transparent and rose-coloured. These crystals deliquesce rapidly in the air. They were analyzed by nitrat of silver to ascertain the muriatic acid, and by carbonat of ammonia for the manganese. Reckoning (after Klaproth) 20.5 of acid in 133 of luna cornea, the crystallized muriat of manganese will contain

Suboxyd . . . . .	38.50
Muriatic acid . . . . .	20.04
Remain for water . . . . .	41.46
	<hr/>
	100.00

When a current of oxymuriatic acid gas is passed through a solution of this salt, it presently stiffens very considerably and nearly the whole becomes a crystalline mass, which again becomes fluid in the air. If this liquid is evaporated, the pungent smell of oxymuriatic acid goes off, black oxyd of manganese falls down, and the remaining solution returns to the state of common muriat of manganese.

*On the Oxydation of Manganese.* The very great disagreement on this subject between the experiments of the most accurate chemists shews the extreme difficulty of determining with any certainty the numbers and proportions of the oxyds of manganese. On the one hand the metal itself and its lowest oxyd have a constant tendency to absorb oxygen from the atmosphere: and on the other hand the highest oxyd will readily give out oxygen at a very moderate encrease of temperature; so that it is very difficult to obtain any quantity of oxyd of this metal of a perfectly uniform state of oxydation throughout.

Dr. John, who is fully aware of these difficulties is inclined to fix the number of definite oxyds of manganese at three, namely, the Green, the Brown, and the Black, of which the green is the lowest oxyd. He thus endeavours to analyze them.

*The Green Oxyd.* Eighty grains of metallic manganese were put in a vessel containing water. The gas obtained was 24 ounce measures and was hydrogen, containing probably some atoms of the metal in solution, as it had a peculiar smell and burnt with a green flame. The gas was given out for a whole day, after which it ceased and was not renewed by heating the contents. The greenish oxyd remaining at the bottom of the water was quickly dried and weighed 92 grains.

This experiment did not much differ from the composition of the green oxyd as the base of the carbonat, and hence the author considers the oxygen as 13 per cent. on the average, and therefore the green oxyd will consist of

Manganese	87.	—	100.
Oxygen	13.	—	14.942
	<hr/>		<hr/>
	100.		114.942

*Brown Oxyd.* This was formed simply by exposing the last mentioned green oxyd to the air till it gained no more weight, and drying it hastily. It was a pure deep brown colour, and consisted of

Manganese	80.	—	100.
Oxygen	20.	—	25.
	<hr/>		<hr/>
	100.		125.
	<hr/>		<hr/>

*Black Oxyd.* This oxyd which is considered as the highest possible in oxygenation, was prepared by dissolving a given weight of metallic manganese in nitric acid, and evaporating the entire solution to dryness in a heat barely sufficient to expell and decompose all the adhering nitric acid, without separating oxygen from the newly formed oxyd. In this manner the black oxyd will contain

Manganese	71.33	—	100.00
Oxygen	28.67	—	40.19
	<hr/>		<hr/>
	100.00		140.19
	<hr/>		<hr/>

This oxyd gives an abundance of oxygen gas at a red heat, and hence the extreme difficulty of driving off all the last portions of nitric acid, and at the same time just avoiding the heat which will change any portion of this oxyd to a lower term of oxygenation.

The following statement of the number and composition of the oxyds of manganese is given as the result of Pr. Berzelius's experiments,\* but the particulars are not mentioned.

1. The lowest oxyd or suboxyd is the grey powder which forms on the surface of metallic manganese when kept in phials closed only by a cork.

2. The green suboxyd of Dr. John described above.

3. The oxyd which is the base of the sulphat of manganese.

4. An oxyd of higher degree.

5. The superoxyd or native peroxyd of manganese.

With regard to these five oxyds, the second, third and fourth are stated to have been analyzed by the author, and to contain on 100 of metal, 14, 28, and 42.16 parts of oxygen respectively, whence, adapting these to the doctrine of definite proportions, the composition of the two extreme oxyds is assumed to be 7.026 on 100 in the lowest and 56.215 in the highest oxyd. The five oxyds therefore will be as follows.

	Oxygen	Metal
1st contains	7.026	to 100
2d	14.052	—
3d	28.104	—
4th	42.156	—
5th	56.208	—

#### MEIONITE.

This mineral has hitherto been found only in minute aggregated crystals. Its primitive form is a strait prism with square bases; it also presents six and eight-sided prisms, terminated by low tetrahedral pyramids. Its colour is a translucent greyish-white, its lustre is vitreous; its longitudinal fracture is foliated in two directions, its cross fracture is conchoidal. It scratches glass.

Before the blowpipe it melts easily into a spongy white glass. It occurs among the substances ejected by Vesuvius, generally lining cavities in white granular limestone.

#### MELILITE.

It occurs in the form of small rectangular parallelipeds and octohedrons of a pale yellow and orange colour, which are often covered with a brownish red crust. It gives fire with steel. When pulverized and put into nitric acid, it becomes perfectly gelatinous. In small fragments it melts before the blowpipe into a transparent glass.

It has been found only near Rome, at Capo di Bove.

#### MENILITE.

It occurs in tubercular masses of a moderate size, striped externally bluish grey and redish brown. Internally it exhibits a hair brown colour, and a glistening somewhat resinous lustre. It is strongly translucent on the edges, and presents a flat conchoidal or splintery fracture. It is hard, brittle and easily frangible.

Its constituent parts, according to Klaproth, are

85.5	Silex
1.	Alumine
0.5	Oxyd of Iron
0.5	Lime
11.	Water and inflammable matter
<hr/>	
98.5	

It is found at Menil Montant near Paris, imbedded in a white slaty rock, and appears to have a considerable analogy with the flints, semi opals and hornstones that are found in the chalk, and in the strata above it.

MORDANT. See DYEING.

MURIATIC ACID. OXYMURIATIC ACID.

CHLORINE. EUCHLORINE.

An immense mass of interesting matter has been bestowed within these last few years on muriatic acid, since the laborious but fruitless attempts of Dr. Henry to discover its base, with which we concluded our former account of this singular substance.

\* An. Chim. tom. 83.

The facts which have been discovered have led to two totally distinct theories on the constitution of this acid, which we shall mention to assist the reader in following the experiments to be related.

1. The opinion of the *acid* nature of this substance, modified by the results of the experiments of Messrs. Gay Lussac and Thenard is the following. Muriatic acid is, like the other acids, a compound of some base (hitherto unknown) and oxygen; it has never been obtained in a separate state, as it is only known to chemists as *Muriatic Acid Gas*, or as forming a part of the alkaline, earthy, or metallic *Muriats*. In the former case, the muriatic acid is intimately combined with about a fourth of its weight of *water* (or of the oxygen and hydrogen which are the elements of this quantity of water), and this is absolutely essential to the existence of muriatic acid *in the gaseous state*, so that under no circumstances can this acid be expelled from its solid combinations, unless such a quantity of water is present as will unite with the gas at the moment of its formation, and will then amount to about a fourth of the weight of the gas. This water exists in muriatic gas in a different mode of combination from that which constitutes the common hygrometrical moisture of gasses, and therefore cannot be separated by solid potash, lime, dry muriat of lime, or intense cold, which are the means successfully used to render the other gasses dry. But when muriatic acid gas is united with any of the alkaline, earthy, or metallic bases, that portion of water which was essential to the acid in an insulated state is no longer retained, and may be expelled from most of them (though often with considerable difficulty) by mere heat.

Oxymuriatic acid on this theory is a compound of muriatic acid and oxygen; and oxymuriatic gas contains oxygen equal to half its volume; but the muriatic acid gas with which it is united is not combined with water, as it is in the insulated state of muriatic acid gas, but if it contains any water, it is only as common hygrometric moisture, which may readily be abstracted by any of the means above mentioned. Hence, in order to convert dried oxymuriatic acid gas to muriatic gas, it is necessary either to abstract oxygen, and to add water in substance; or else to add hydrogen, which by uniting with the excess of oxygen may produce water, this, as before mentioned, being essential to the constitution of muriatic acid gas.

2. The theory adopted by Sir H. Davy, is the following.

Oxymuriatic acid is a substance hitherto undecomposed, and therefore must at present be considered as an element; it contains no oxygen, at least none has ever been extracted from it; it unites with most metals and salifiable bases, forming the *muriats*, which therefore are not (like the sulphats, nitrats, &c.) compounds of an *oxydated* base and an acid, but are composed merely of the base and of oxymuriatic acid. Thus for example, common salt, or muriat of soda, when perfectly dry, is according to this hypothesis composed, not of soda and muriatic acid, but of sodium and oxymuriatic acid, and so of the rest. Oxymuriatic acid will however unite with oxygen, forming a very singular compound, whose properties have been discovered by Sir H. Davy. This eminent chemist gives the name of *Chlorine* to oxymuriatic acid, and of *Euchlorine* to the compound of oxymuriatic acid and oxygen, which will be presently described.

Muriatic acid according to this theory, is a compound of oxymuriatic acid and hydrogen in equal volumes; it contains no water of composition, for none can be procured from it, unless by substances that contain oxygen, and the quantity of water produced is exactly equal to the oxygen contained in the substance employed, added to the hydrogen supposed to exist in the muriatic acid gas. The salts called *muriats* are, when perfectly dry, composed of oxymuriatic acid and the respective bases, but not in the state of oxyds; but as soon as water is added to a dry muriat, a double decomposition takes place, the oxygen of the water goes to the base of the muriat converting it to an oxyd, the hydrogen of the water unites with the oxymuriatic acid, converting it to muriatic acid, and the compound now becomes really a muriated oxyd. On the other hand if this muriated oxyd is again dried in the heat of ignition, the salt is again decomposed, the hydrogen of the muriatic acid escapes with the oxygen of the oxyd in the form of water; and the salt returns to the state of a simple binary compound of oxymuriatic acid and the base.

We shall now give a short abstract of several of the most important series of experiments on these compounds, beginning with those of Messrs. Gay Lussac and Thenard.<sup>a</sup>

The first object of enquiry is the existence of water in gasses. When common air is en-

<sup>a</sup> Recherches Physico-chimiques, tom. ii.

closed over mercury in contact with dry potash, or muriat of lime, it is universally known that these substances absorb the moisture that the air held in solution, and leave it perfectly dry. If instead of potash or muriat of lime, a little *fluoboracic acid gas* (which article see) be added, an immense cloud of dense vapour is produced owing to the combination of this acid gas with the moisture of the air. But if fluoboracic gas be added to another portion of air that has previously been in contact with potash, or with muriat of lime, no cloud whatever takes place. Hence it is inferred, that the air naturally contains a quantity of moisture dissolved in it, (termed by these chemists *hygrometric water*) which is simply absorbed by the potash, fluoboracic gas, or any other substance that has a strong affinity with water. If the air is exposed to an intense cold, it also parts with all its hygrometric water, which is a more convenient method of operating in many experiments, as it does not require the presence of any foreign substance. So delicate a test of hygrometric moisture is the fluoboracic gas, that if only a fiftieth part of moist air be added to air hygrometrically dried, this added portion will be made sensible by a vapour on introducing a little of the gas.

By employing this gas as a test of hygrometric water, it was found that all the gasses insoluble (or nearly so) in water, were capable of containing a considerable portion of hygrometric water separable by the means above mentioned.

Some of the gasses soluble in water, such as oxymuriatic acid, carbonic acid, and sulphureous acid gas, also contain a portion of hygrometric water, but this must be always less in proportion to the solubility of the gas, since the contact of water constantly tends to make them assume the liquid state.

On the other hand, muriatic acid gas, even when procured by boiling liquid muriatic acid, and without being subjected to any drying process, gives no vapour whatever, either when exposed to intense cold, or to fluoboracic acid, and hence the authors infer, that muriatic acid gas contains no hygrometric water.

Nevertheless, these chemists assert that muriatic acid gas does actually contain a very large portion of water, which is not separable from it by those means that detach hygrometric water, but is absolutely essential to its constitution as long as it retains its gaseous form, and therefore, muriatic acid gas cannot be expelled from the dry muriats, unless sufficient water is present to unite with the gas as it forms, and to constitute about a fourth of its weight. The

following experiments are given in support of this opinion.

A mixture of dry muriat of silver and melted boracic acid was strongly heated in a coated iron tube, but no gas was expelled, except the common air of the apparatus. On the other hand a similar mixture was heated in an iron tube, and when scarcely red-hot, some steam was passed through it from water boiling in a small retort connected with the apparatus. Immediately a large quantity of muriatic acid vapour was given out, the muriat of silver was completely decomposed, and only borat of silver remained.

Some charcoal previously ignited in a strong forge furnace was mixed with twice its weight of melted muriat of silver, and the mixture put into a porcelain retort and heated. When red-hot, a little muriatic acid and inflammable gasses were given out, but this soon ceased, and though the heat was raised so high as to soften the retort, no more gas was obtained. The greater part of the muriat of silver was found unchanged in the retort.

On the other hand, similar materials were heated in an earthen tube, and the steam of water was transmitted through them when scarcely red-hot. A great abundance of muriatic gas was expelled, and the silver was entirely reduced. The reason that some decomposition took place in the former experiment, was obviously owing to the great difficulty of expelling by mere heat every particle of water existing in charcoal; for charcoal not previously ignited when heated with muriat of silver, immediately disengages muriatic acid gas, and the silver is reduced.

Similar experiments were made with vitrified boracic acid, and fused muriat of barytes. Very little muriatic acid was obtained, and after the utmost effect of the fire, the boracic acid and the muriat of barytes were found in distinct strata nearly unchanged. On the other hand, the transmission of steam through the same materials, expelled all the muriatic acid at a low red heat, and the residue was borat of barytes.

The muriats of strontian, soda and lime gave similar results, the latter however produced rather more muriatic gas without the intervention of the water, owing probably to the very powerful attraction of the muriat of lime for moisture, which makes it hardly possible to expell the last portions by mere heat.

As a proof of the retention of some moisture by fused muriat of lime, as well as by vitreous phosphoric acid, and by charcoal and some other substances after being strongly ignited, it is

found that when heated with clean iron filings, they all give more or less of hydrogen gas.

This action of water on the muriatic acid of the muriats is therefore so great, that the dry muriats which resist decomposition at the highest temperature by boracic or phosphoric acids, are readily decomposed by the same reagents, with the intervention of aqueous vapour at a very low red heat. Nor is this all, for, as will be presently mentioned, the dry muriat of magnesia formed by passing oxymuriatic acid over calcined magnesia will give up none of its acid by mere heat, but will readily yield it by the addition of aqueous vapour alone, without the assistance of any other base. This however is not the case with most other muriats, for these are not decomposed by water alone, though readily so by water and a fixed base.

The decomposition of muriat of soda by sand in this manner is interesting on many accounts, and possibly (as the authors observe) might afford an economical mode of obtaining the alkali from salt. Two parts of fine sand, and one of fused common salt were mixed and put into a porcelain tube and heated to redness. Steam was then passed through from a small retort of boiling water connected with the tube, and a great abundance of muriatic acid vapour escaped at the other extremity. This was kept up for five hours, at the end of which the vapours were still acid. On examining the contents of the tube when cold, they were found to be an uniform opake frit, tasteless and insoluble in water and acids, but readily dissolving with a little addition of alkali. It still contained some undecomposed salt, but perfectly combined and vitrified with the sand.

Though the soda was not in this experiment actually obtained separate, there is no doubt but that it had been sufficient to dissolve the sand by fusion. This fact may perhaps be of advantage to the glass-maker. The other earths will also furnish a means of detaching the acid from salt. Thus much muriatic acid is given out by calcining balls of clay and salt, as long as the clay retains any moisture.

Many of the metallic muriats equally resist decomposition without the intervention of water, and yield their acid when moistened. Some calomel and recently calcined charcoal were strongly heated *per se* in a tube, but without any effect; but when common unprepared charcoal was used and the heat scarcely reached a cherry-red, much muriatic acid was given out, and the mercury was entirely reduced. Corrosive sublimate had the same effect as calomel.

The next object of these chemists was to as-

certain the proportion in which water enters into the composition of liquid or gaseous muriatic acid. For this purpose the following experiments were made: 60. parts of oxyd of silver were combined with 15. of muriatic acid gas, and 71.3 of fused muriat of silver were produced. Hence as fused muriat of silver parts with none of its acid at the temperature of fusion, it was concluded that the difference of weight between that of the oxyd of silver and acid gas employed, and that of the fused muriat of silver produced, (amounting to 3.7) was the amount of the water combined with the muriatic acid gas before its union with the oxyd of silver, and hence this acid gas contains about a fourth of its weight of combined water, though as already mentioned, no water can be extracted from it by the common means of freeing gasses from hygrometric moisture. Another computation was made in the following way. Oxyd of silver was prepared by adding pure potash to pure nitrat of silver, and it was dried at the heat of a boiling solution of muriat of lime. Some of this oxyd was separately heated *per se* till the silver was reduced, and it was afterwards found to contain no moisture, and by estimating the oxygen given out in the reduction, the oxyd was found to be constituted in the proportion of 100. of silver to 7.6 of oxygen. The oxyd being thus previously analyzed, a given weight was combined with a known weight of muriatic acid gas, and the fused muriat of silver resulting from the mixture being weighed, this salt was estimated to consist of

100.00 Silver  
7.60 Oxygen  
25.71 Muriatic acid

A given quantity of muriatic acid gas dissolved in water was then precipitated by nitrat of silver, and (estimating from the above data) muriatic acid gas was found to contain 24 per cent. of water, which nearly coincides with the former experiment.

A further proof of the existence of water in muriatic acid gas, is stated by these chemists to be furnished by the mutual action of hydrogen and oxymuriatic acid gas, and as the particulars of these experiments (whatever be the inference) are most interesting, we shall give them with some minuteness.

First to determine the specific gravity of oxymuriatic gas, a retort was partly filled with common salt, oxyd of manganese, and dilute sulphuric acid, and the oxymuriatic acid gas obtained by gently heating these materials was passed through a large quantity of dry muriat

of lime, and thence through a tube, to the bottom of a dry matrass full of common air. As the acid gas is much heavier than common air, and as the tube dipped quite to the bottom of the matrass, in half an hour the whole of the common air was expelled, and the oxymuriatic acid gas had taken its place. The whole was then weighed, and by making the proper corrections, the specific gravity of the oxymuriatic acid gas was found to be 2.47 common air being 1. This experiment was repeated twice, the acid gas being analyzed afterwards in order to ascertain that it contained neither common air, nor carbonic acid.

Oxymuriatic acid gas was placed in contact with hydrogen in two modes, by ammonia, and by pure hydrogen gas.

In the former mode, a narrow necked matrass filled with oxymuriatic acid gas was dipped into liquid ammonia. In a few minutes the whole of the gas was decomposed, and in its place a quantity of azote was produced, equal to a third of the volume of the oxymuriatic gas.

Hence, as ammonia consists of one part in bulk of azote, and three of hydrogen, it follows that the oxymuriatic acid gas must have absorbed three times the bulk of the azote, or in this case, as much hydrogen as the acid gas itself: hence too (as two volumes of hydrogen unite with one of oxygen to produce water) the oxygen in the acid gas is inferred to be equal to half its bulk. As this experiment is attended with some risk of explosion, it is proper to use the liquid ammonia in a dilute state, to introduce but little of it at a time into the matrass, and not to shake them together.

The other mode of making the experiment is by mixing oxymuriatic acid gas and hydrogen gas, and exposing them with caution to the sun's rays. For this purpose a glass matrass was selected, the neck of which entered the neck of another balloon matrass of the same capacity, and was made to fit by grinding.

One of the vessels was filled with oxymuriatic acid gas, and the other with an equal volume of hydrogen, and they were brought in contact by thrusting the smallest neck into the larger, and the juncture was made still firmer by cement. This apparatus was exposed to the diffused solar light for two or three days, during which the greenish-yellow of the oxymuriatic acid gas gradually disappeared. The process was finished by putting the apparatus into the sun's direct rays for an hour or two. The apparatus was then opened under mercury, and no absorption took place, shewing that the

bulk of the gasses remained the same, but on introducing a little water, the whole gas was immediately condensed into liquid muriatic acid, with the exception of a few remaining bubbles of gas, supposed to be the azotic impurity of the gasses employed.

Some care is required in making this experiment. If the mixed gasses are at first exposed to the direct rays of the sun, the whole detonates in a few minutes with a violent explosion. On the other hand, if the vessel is set in a perfectly dark place, no action whatever appears to take place in several days; so that if after this it is placed in a bright sunshine, it detonates as violently to all appearance, as it would do on the first moment of mixture. To succeed therefore in this experiment, the vessel should be set in as light a place as possible, but protected from the direct sunshine, till the decomposition appears nearly completed, and the peculiar colour of the oxymuriatic acid gas is gone, after which it may be as well to complete the process by a few hours in the direct sunshine.

It appears therefore that one volume of oxymuriatic acid gas and one volume of hydrogen, produce by their mutual action two volumes of muriatic acid gas, without any other gas being generated, or any water deposited. The specific gravities of these gasses is given by the authors as follows: (common air being unity) viz. Oxymuriatic acid gas 2.47 Oxygen gas 1.1034. Hydrogen gas 0.0732.

Hence the absolute weight of 247 grains of oxymuriatic acid gas (supposing it to consist of equal volumes of oxygen and muriatic acid freed from water of composition) will be

Grains.
55.17 Oxygen
191.83 Dry muriatic acid
<hr style="width: 20%; margin: 0 auto;"/>
247.00 grains of oxymuriatic acid gas

And adding to this 7.32 grains of hydrogen (being the weight of an equal volume of this gas) the muriatic acid gas produced will be 254.32 grains, and the oxygen and hydrogen of this will together amount to 62.49 grains, which is inferred to be in the state of water in union with the muriatic acid gas, and is 24.57 per cent. of its weight.

Since muriatic acid gas results from the union of oxymuriatic acid gas and hydrogen, it may be inferred that it contains exactly that proportion of oxygen and real acid sufficient to convert the metals into muriats, and it will be totally absorbed by those metals that have the strongest

affinity for oxygen. Thus if clean iron turnings are heated to low redness in a gun-barrel, and muriatic acid gas is passed through, pure hydrogen gas is disengaged, and the iron is changed to muriat of iron. But it has been found by Richter and Gay Lussac, that in all similar metallic salts, the acid and oxygen bear the same proportions to each other; and hence the acid and oxygen must be in the same ratio in muriat of iron as in muriat of silver, or (from the analysis of the latter salt) as 7.60 oxygen to 25.71 acid. These therefore must be the respective quantities of oxygen and acid in muriatic acid gas, since it forms muriat of iron by simple union with this metal. On the other hand, the hydrogen is found by the experiment of hydrogen and oxymuriatic acid gas to be in the same proportion to the oxygen in muriatic acid gas as that which constitutes water, which for 7.6 oxygen will require  $1.034 \text{ hydrogen} = 8.634 \text{ water}$ : and if this (from the analogy with muriat of silver) requires 25.71 acid, the whole will constitute  $25.71 + 8.634 = 34.344$  muriatic acid gas, of which the water constitutes almost exactly a fourth of the weight.

The next object of enquiry with these eminent chemists was to determine the action of dry oxymuriatic acid gas on various bodies. The constitution of this gas is assumed, as already mentioned, to be muriatic acid freed from its water of composition, in gaseous combination with its own volume of oxygen. It may be decomposed in its gaseous state in three ways: 1st, by those substances which absorb it entirely, such as the metals, sulphur, and phosphorus. 2dly, by those oxyds (earthy or metallic) which combine with the dry muriatic acid, and thus disengage the oxygen of the gas: and 3dly, by hydrogen or substances containing hydrogen, which by uniting to the oxygen of the oxymuriatic acid gas will furnish that quantity of water necessary to cause the muriatic acid to assume the gaseous form.

The first method of decomposing oxymuriatic acid gas is by placing it in contact with most of the metals, whence the metallic muriats are produced.

Sulphur also forms with oxymuriatic acid gas a compound first discovered by Dr. Thomson, and which is considered by Berthollet as a triple compound of muriatic acid, oxygen, and sulphur. Many of the metallic sulphurets furnish the same compound.

Oxymuriatic acid gas is also decomposed by phosphorus, and the result is a very singular compound which was first described by Sir H.

Davy, who obtained it by heating phosphorus in the gas. It has been procured by the French chemists in the following manner: some phosphorus was put at the bottom of a glass tube closed at one end, and over it about double the weight of calomel. A gradual heat was applied, the phosphorus slowly sublimed through the calomel, and almost immediately the peculiar liquid in question was produced, which condensed in a small receiver adapted to the open end of the tube, but closed from the access of external air. This peculiar liquid is limpid, fuming, colourless, acid, and very caustic. When exposed to the air it is entirely decomposed, and phosphorus is deposited. Water partly dissolves it, and phosphorus separates. Potassium burns in it vehemently, and muriatic acid gas is formed. When this liquor is heated and its vapour passed through heated iron filings it is totally decomposed, no gas is given out, and the iron is changed to muriat and phosphuret of iron. Corrosive sublimate answers as well for obtaining this liquid as calomel.

The second method of decomposing oxymuriatic acid gas is by the action of some substance which absorbs the acid and allows the oxygen to escape. Lime answers this purpose. Some pure and strongly ignited lime was intensely heated in a porcelain tube, and dry oxymuriatic gas was passed through. The gas was almost totally decomposed, much oxygen gas was evolved, and the tube, when cold, was found to contain a fused mass of muriat of lime.

A similar decomposition took place by passing the gas through calcined magnesia; much oxygen was given out, and a dry neutralized muriat of magnesia remained. This muriat did not part with its acid at a very intense heat; but as soon as it was moistened it became similar to the common muriat prepared by dissolving magnesia in liquid muriatic acid; and like this it now yielded up its acid at a very moderate ignition.

The third mode of decomposing oxymuriatic acid gas is by hydrogen, either singly or holding sulphur, &c. in solution, or in the form of water. The decomposition by hydrogen alone has been fully described.

Sulphuretted hydrogen, mixed with oxymuriatic acid gas, gave an immediate deposition of sulphur, and muriatic acid gas was produced in equal volume to the gasses employed.

Phosphuretted hydrogen decomposed it with equal rapidity.

Carburetted hydrogen decomposed it only



after some days exposure to light, and charcoal was deposited.

The vapour of water and oxymuriatic acid gas were both together transmitted through a red-hot porcelain or luted glass tube, and the products were oxygen gas and liquid muriatic acid. When the tube was kept very hot and the vapour of the water was abundant in proportion to the oxymuriatic acid gas, scarcely a particle of the latter escaped decomposition.

The converse of these experiments, and what the authors consider as a proof of the justness of the theory derived from them, was the failure to decompose oxymuriatic acid gas by other substances in themselves greedy of oxygen, but either containing no hydrogen, and therefore not being able to produce water with the oxygen of the oxymuriatic acid gas, to enable it to become gaseous muriatic acid; or else, being of such a nature when oxydated as not to form chemical compounds with muriatic acid deprived of water. The substances employed were sulphurous acid gas, carbonic acid, nitrous oxyd, and nitrous gas, all carefully freed from hygrometric moisture; and these were mixed with equally dry oxymuriatic acid gas, and kept for several days exposed to light, but the green colour of the oxymuriatic gas was unaltered, and on shaking the mixture with mercury it was totally absorbed, leaving unchanged the gas with which it had been mixed.

The dry sulphites of barytes and lime were kept for five or six days in contact with dry oxymuriatic acid gas, but without any change; though on moistening them, the products were a mixed sulphat and muriat of the earth employed, and a disengagement of sulphureous acid gas.

We shall conclude our account of the experiments of Messrs. Gay Lussac and Thenard, by the short summary which they have given of the leading facts.

1. Oxymuriatic acid gas when singly exposed to the sun's rays, is not changed, but when it is at the same time in contact with water it disappears, and is converted into muriatic acid gas and oxygen.

2. Hydrogen gas and oxymuriatic acid gasses, in equal volumes, when exposed to solar light, combine into muriatic acid gas, without change of volume or deposition of water.

3. Pure charcoal has no effect on oxymuriatic acid gas at any temperature, but if it contains hydrogen muriatic acid gas is produced, and if it contains water, both muriatic acid gas and carbonic acid are generated.

4. Phosphorus absorbs oxymuriatic acid gas, and produces a peculiar liquid.

5. The same liquid is obtained by treating the muriats of mercury with phosphorus, and then the mercury is reduced, but no muriatic acid is disengaged.

6. Sulphur absorbs oxymuriatic acid gas, producing that peculiar compound first discovered by Dr. Thomson.

7. The metallic sulphurets have the same action as water.

8. All the metals will combine with oxymuriatic acid gas, and form thereby metallic muriats. Some of the metals, such as zinc and iron, are powerfully acted on by muriatic acid gas, and hence result metallic muriats, similar to those obtained from the oxymuriatic acid, but also with the production of as much hydrogen as the volume of muriatic acid gas absorbed.

9. None of these muriats can be decomposed by pure charcoal, by vitrified boracic acid, or by glass of phosphorus.

10. On the other hand, all these muriats may be decomposed by the above substances with the assistance of water, or by carburetted hydrogen, and hence by animal and vegetable substances. The metallic muriat with water and charcoal produces muriatic acid gas, carbonic oxyd, and the metal is reduced: the muriat with water and phosphoric acid, gives muriatic acid gas, and the metallic phosphat: the muriat with hydrogen gives muriatic acid gas, and the metal is reduced.

11. The muriats of barytes, strontian, lime, potash, soda, and magnesia, when quite dry, are not decomposed by the dry boracic and phosphoric acids, but are readily decomposed by them when moisture is present. Charcoal however in neither case decomposes them.

12. The muriats of glycine, yttria, alumine, zircon, and silix, would probably agree in properties with those last mentioned, if they could be obtained free from water.

13. When muriatic acid gas and dry oxyd of lead are mixed together at a moderately high temperature, the gas is absorbed, and muriat of lead and water are produced: the same result is obtained with the other metallic oxyds.

14. A similar result with the last is obtained by using barytes, strontian, and lime, instead of oxyd of lead.

15. Common salt cannot be decomposed at any temperature by sand or alumine, but is easily decomposed by either of them when

moistened. The same may be said of the muriats of barytes, potash, strontian, and lime.

16. Oxymuriatic acid gas, when in contact with liquid ammonia, disappears, muriat of ammonia is formed, together with azote, equal in volume to a third of the acid gas absorbed.

17. Sulphureous acid gas, nitrous oxyd, and nitrous gas, have no action on oxymuriatic acid when dry, but with contact of moisture the decomposition is sudden, and the above three gasses become oxygenated.

18. The dry sulphites have no action on oxymuriatic gas, but when moisture is admitted the action soon begins, sulphureous acid, a muriat, and a sulphat are formed.

19. When Libavius's liquor (or dry muriat of tin) is put in contact with ammonia over mercury the gas is absorbed, no other gas is given out, and a white solid is produced, which when heated, sublimes entire. Ammonia therefore will not separate oxyd of tin from this solution, unless water is added, and then the oxyd separates immediately.

20. When phosphorus is treated by oxymuriatic acid gas, a liquid and a solid compound are formed, which will unite to ammonia into a singularly fixed substance, but without obvious decomposition, unless water is added, in which case ammonia is expelled, and muriatic and phosphoric acids are produced.

21. Oxymuriatic acid gas absorbs thrice its volume of ammoniacal gas, a dry muriat of ammonia is produced, and azote about equal to a tenth of the entire volume is given out.

We shall now proceed to give some of the leading experiments on oxymuriatic acid and its compounds, from which the most original and inventive chemist of our own times has raised a theory that at present divides the chemical world.<sup>b</sup>

The opinion advanced by Sir H. Davy on the nature of these substances is, that oxymuriatic acid is a simple undecomposed substance containing no oxygen, but capable of combining with many bases into compounds, in many respects analogous to oxyds, and often giving out heat and light during the combination. To avoid confusion in this mode of considering the subject, and the impropriety of expressing in its name the presence of oxygen, the inventor of this theory has given to oxymuriatic acid the term *Chlorine*, derived simply from the green colour which it possesses when in a gaseous form. On the other hand, *Muriatic Acid* is a compound of chlorine and hydrogen in

equal volumes, and contains no water of composition when in the form of gas.

*Chlorine or Oxymuriatic Gas.*

This substance is of a yellowish green colour, when gaseous. Its sp. gr. is to that of hydrogen, as 33.5 to 1. and 100 cubical inches at a mean temperature and pressure weigh 76 to 77 grains. Water at 60°. dissolves about double its volume of this gas. When an inflamed taper is introduced into a phial filled with it, the light continues, but of a dull red colour, and a dark carbonaceous smoke arises from the flame. Many of the metals introduced into it in thin leaves or in powder take fire, and burn spontaneously at a common temperature. Such are copper, tin, arsenic, zinc, antimony, potassium, and sodium. Phosphorus burns in it spontaneously with a pale white light, producing a white volatile powder. Sulphur melted in it does not burn, but forms with it a volatile red liquor.

Chlorine is not changed by the action of electricity if pure.

It is not altered by any action of heat or cold, but its aqueous solution freezes at about 40°. Fahr.

It is capable of holding hygrometric water in solution, which may be separated by muriat of lime.

Chlorine when quite dry does not change vegetable colours, but when moisture is present the colours are speedily destroyed or brought to a dull yellow.

Chlorine unites with oxygen forming a peculiar compound, which will be presently noticed.

When potassium is introduced into chlorine gas, a very vivid inflammation ensues, and a dry salt results, which is the same as fused muriat of potash. One grain of potassium absorbs about 1.1 cubic inch of the gas. If the potassium is first oxydated by combustion in oxygen gas, and the dry oxyd thus produced is afterwards gently heated in chlorine, as much oxygen is expelled from the oxyd as was at first absorbed by the potassium, and the residue is muriat of potash, exactly the same in quantity as would have been produced by the simple combustion of the potassium in chlorine. No water is produced in this experiment, provided care be taken to exclude the crust of potash on the surface of the metal; and hence the author explains it to be an example of decomposition of the oxyd of potassium by simple affinity, the chlorine uniting with the metallic base and the oxygen being expelled, Hence

<sup>b</sup> Davy, Elements of Chemical Philosophy. Phil. Trans. for 1809, 10, 11, 12.

the author of the experiment considers the salt dry muriat of potash, to be in fact a compound of chlorine and potassium, which agreeably to the nomenclature he has adopted, he terms *Potassane*.

When sodium is used similar appearances take place, chlorine is absorbed (but in nearly twice the quantity of that absorbed by an equal weight of potassium) all the oxygen united with the oxyd of sodium is expelled, and the compound *Sodane* is produced, which is identical with fused muriat of soda.

When sodane is heated with potassium, sodium is sublimed, and this furnishes the easiest method of procuring this metal.

Two parts of potassium furnish one of sodium.

When potassium is exposed to muriatic acid gas dried by muriat of lime, it immediately becomes covered with a white crust, no inflammation ensues, but the gas is totally absorbed, and if proper proportions of each substance be used, the whole of the potassium is changed to muriat of potash (as with chlorine and potassium), but with this difference, that when muriatic acid gas is employed, there is a gaseous residue consisting of hydrogen, amounting to a third of the volume of the muriatic gas employed.

The muriat of potash thus produced will furnish with nitrat of silver exactly the same weight of muriat of silver as the same quantity of muriatic acid gas simply absorbed by water, and then decomposed by nitrat of silver. This fact, which was at first brought forward as a proof of the existence of combined water in muriatic acid gas, will obviously admit of an equally consistent explanation on the hypothesis, that this gas consists of chlorine and hydrogen, and that the dry muriats are compounds of chlorine and the base, singly and not oxydated.

It has been stated that when the oxyds of potassium are heated in chlorine, muriat of potash (or the compound of chlorine and potassium) is produced, and as much oxygen is expelled as was before contained in the oxyd. The same takes place when the oxyds of barium, strontium, and calcium, (or in other words, the *earths* barytes, strontian, and lime) are heated with chlorine; the dry muriated earth is produced, and oxygen is expelled.

The compounds produced by the action of chlorine and phosphorus are peculiarly interesting. If a small exhausted retort furnished with a stop-cock is filled with dry chlorine gas and some phosphorus added, the mixture kindles and burns with a white flame. The chlo-

rine is totally absorbed, for when the stop-cock is opened, a fresh quantity of chlorine, nearly as much as would have filled the vessel, will enter. In this way, one grain of phosphorus will absorb nine cubic inches of chlorine. A white sublimate collects at the top of the vessel, and a limpid fluid trickles down the sides. The sublimate gives fumes of muriatic acid when exposed to air, and when moistened is converted to phosphoric and muriatic acids. This sublimate is a non-conductor of electricity, and when heated, sublimes unchanged at a less heat than boiling water: when touched with a lighted taper it inflames, and when passed through a red-hot glass tube with oxygen, phosphoric acid is produced, and chlorine is evolved. The vapour of this sublimate reddens dry litmus. It absorbs dry ammoniacal gas with much heat, and the result is a compound insoluble in water, without taste or smell, which is undecomposable by acid or alkaline solutions, and is not volatile at an intense red-heat in close vessels, but heated in the air it produces phosphoric acid. Sir H. Davy considers the sublimate as composed of 134 of chlorine to 20 of phosphorus, as deduced from the quantity of muriat of silver which it produces with nitrat of silver. He terms this sublimate *Phosphorana*.

It has been mentioned that along with this sublimate a limpid fluid is produced. This fluid is obtained in greater abundance by subliming phosphorus through a stratum of heated corrosive sublimate or calomel in a glass tube. It is a limpid colourless fluid of the specific gravity of 1.45. It emits acid fumes when exposed to *moist* air, but not to dry: and it does not redden litmus paper unless it be damp. The vapour arising from heating this fluid is highly combustible. When this fluid is put in contact with dry chlorine, it is converted to *phosphorana*, the last mentioned substance, and when in contact with ammonia, phosphorus is produced, and the same compound as that formed by phosphorana and ammonia. This fluid analyzed by nitrat of silver is composed, according to Davy, of 20 of phosphorus and 67 of chlorine. It has therefore only half the chlorine of the former compound, and is termed *phosphorane*.

Chlorine will unite with sulphur into a peculiar compound, which was first produced by Dr. Thomson, by passing chlorine over flowers of sulphur, and considered by him as sulphuretted muriatic acid. It is obtained also

• Phil. Trans. 1809 and 10. Davy's Elements.

more expeditiously by heating sulphur in a retort filled with chlorine. The compound in question is a fluid volatile below 200°, and distills into the cold part of the retort. Its colour by reflected light is red, but yellowish green in transmitted light. It smokes when exposed to air. Its specific gravity is 1.6. It does not redden dry litmus. When water is added, it becomes turbid and strongly sour with sulphuric acid.

Ten grains of sulphur absorb nearly 30 cubic inches of chlorine, which is nearly in the proportion of 30 sulphur to 67 chlorine. Considering this as a compound of sulphur and chlorine, Sir H. Davy calls it *Sulphurane*.

The appearances that take place on the union of chlorine and hydrogen have been already fully described. One volume of hydrogen unites to 1 volume of chlorine, or 1 in weight of hydrogen to 33.5 chlorine, and the product is 2 volumes of muriatic acid gas. This elementary experiment has been explained according to each theory of muriatic acid as has been already described.

Chlorine has no action whatever on carbon even when assisted by common ignition or by the most intense power of voltaic electricity, provided the chlorine be previously dried, and the charcoal ignited in a strong heat.

The action of chlorine on most of the metals is very powerful, many of them burning with a brilliant flame when introduced in a divided state into chlorine gas. The products vary considerably in consistence and sensible properties, being in some instances solid, in others forming dense fluids, which have been long known under the name of metallic butters.

Thus the *Butter of Arsenic* is produced by the action of chlorine on metallic arsenic; the *Butter of Antimony* by chlorine and antimony, &c. The compound of chlorine and mercury is corrosive sublimate; tin and chlorine furnishes that singular fluid called Libavius's liquor. If this liquor is confined in ammoniacal gas, the ammonia is absorbed with much heat, and a grey solid is produced, which when heated is entirely volatilized in very pungent fumes; ammonia therefore alone does not decompose this liquor, but when water is added a peroxyd of tin is deposited, and the liquid becomes a solution of muriat of ammonia. All the compounds of chlorine and of the metals are decomposed by water, the metal being partially separated in the form of oxyd and the liquid containing muriatic acid. This is explained by

Sir H. Davy on the hypothesis, that the water is decomposed on the compound of chlorine and the metal, the oxygen of the water passing to the metal, and its hydrogen uniting with the chlorine to form the muriatic acid which is then generated.

The metallic *oxyds* are most of them acted upon by chlorine, but with great difference in the appearances. The oxyds of lead, silver, tin, copper, antimony, bismuth, and tellurium are decomposed in a heat below redness; the oxyds of cobalt and nickel require a red heat; the red oxyd of iron is not at all acted on, but the black oxyd is with ease: arsenical acid is not altered by being heated in chlorine, but the white oxyd is readily decomposed. In the cases where oxygen was given off, it was found to be pretty exactly the same as that which previously existed in the oxyd.

All these compounds have received new names in the author's nomenclature with the termination *ane*; the compound of silver and chlorine being *argentane*; butter of antimony, *antimonane*, &c.

CHLORINE AND OXYGEN. EUCHLORINE. This curious compound of chlorine and oxygen was discovered by Sir H. Davy in 1811.<sup>d</sup>

Chlorine prepared from pure oxyd of manganese is uniform in its properties, but the gas obtained by muriatic acid and the salts commonly called hyperoxymuriats, differs very much in its properties, according to the circumstances of its preparation. When much acid is employed to a small quantity of salt, and the gas is collected over water, the water becomes tinged of a lemon colour, but the gas is pure chlorine the same as that from manganese. But when the gas is collected over mercury, and is procured from a weak acid and a great excess of the salt by a low heat, its colour is a deep greenish yellow, and it possesses properties totally different from pure chlorine. This gas termed Euchlorine by the discoverer, is distinguished for the facility with which it explodes, often merely on being transferred from one vessel to another, and always by a very gentle heat, and hence it is not safe to operate on large quantities. By explosion in close vessels, it is resolved into chlorine and oxygen. This gas is partially decomposed by water, and oxygen is set free, but it is very little so by mercury.

On the other hand mercury readily absorbs pure chlorine, and therefore the two gasses may be separated by agitation with mercury,

<sup>d</sup> Ph. Trans. for 1811, and Davy's Elements.

which forms corrosive subimate with any portion of chlorine with which the gas is mixed, and the euchlorine remains pure.

Euchlorine is more yellow than chlorine, and its smell is like that of burnt sugar. Its specific gravity is to that of hydrogen as 33 to 1, and 100 cubic inches of it weigh from 74 to 75 grains. 50 parts of euchlorine after detonation expand to 60 parts, of which about 40 are chlorine and 20 pure oxygen, and hence it is composed of two parts in volume of the former to one of the latter, and the oxygen which it contains is condensed to half its volume.

Water takes up about 8 or 10 times its volume of euchlorine, but this cannot be again expelled without decomposition.

When euchlorine is detonated with twice its volume of hydrogen, there is an absorption of more than  $\frac{1}{3}$ , and a solution of muriatic acid is formed: when the euchlorine is in larger proportion there is also an evolution of oxygen.

None of the metals that burn in chlorine act upon euchlorine at common temperatures, but when the oxygen is separated, or when the heat is raised, they then inflame.

Thus let a vessel be exhausted and filled with euchlorine and some brass foil introduced, and no action will ensue, but on passing up a little nitrous gas the oxygen is removed, and then the chlorine begins to act upon the brass and inflame it.

Phosphorus explodes in euchlorine, and the product is phosphoric acid and oxymuriat of phosphorus or *phosphorane*.

When euchlorine is mixed with muriatic acid gas there is a gradual diminution of volume, chlorine gas is formed, and a dew appears on the sides of the vessel.

Euchlorine even when freed from hygrometric water reddens vegetable blue colours and then destroys them, which circumstance, together with its absorbability by water, and the acrid taste of its solution would lead to the opinion that euchlorine has somewhat of an acid nature.

**CHLORINE AND AZOTE.** A very peculiar compound of these two elements, which appears to be one of the most powerful detonating substances hitherto known, is described under the article *Azotized oxymuriatic acid*.

**CHLORINE AND CARBONIC OXYD.** Some facts relating to the mutual action of these substances have been observed by Mr. John Davy, which require a short notice.

When equal volumes of these gasses (both

perfectly dried by fused muriat of lime) are mixed together in an exhausted glass globe, with a stop-cock, and every precaution taken to exclude moisture, and exposed for about a quarter of an hour to bright sunshine, the colour of the chlorine disappears, and on opening the stop-cock over dry mercury, an absorption of one half of the original bulk takes place, and the remaining gas is a peculiar compound to which Mr. J. D. gives the name of *Phosgene Gas*. This gas is intolerably pungent and suffocating, and reddens litmus. Its specific gravity, inferred from that of its constituent parts, is very great, so that 100. cubic inches weigh 105.97 grains.

Water rapidly changes this gas into the carbonic and muriatic acids. Many of the metals heated in this gas entirely decompose it, though without ignition or explosion in any instance: a compound of the metal and chlorine is formed, and the carbonic oxyd remains unaltered, and then resumes its original bulk, which is equal to that of the entire gas before decomposition. Sulphur and phosphorus sublime in the gas unaltered. This gas is remarkable for the large quantity of ammoniacal gas which it condenses, being as much as four times its volume. The product is a white neutral salt of a pungent saline taste, effervescing with the strong acids, and giving out muriatic and carbonic acid.

The nature of this ammoniacal compound is somewhat doubtful, and has been the subject of controversy between Mr. J. Davy and Mr. Murray, but it is not doubted that chlorine and carbonic oxyd mixed together and exposed to the sun's rays, do really combine into the very dense gas described by Mr. J. D. whose properties are different from those of any other known gaseous compound.

**MURIATIC ACID GAS AND AMMONIA.** It has been already observed that most of the facts relative to the chemical action of muriatic and oxymuriatic acids may be explained with equal plausibility, either on the hypothesis that dry muriatic acid gas consists of muriatic acid and water of composition; that the dry muriats consist of the oxydated base united to muriatic acid alone, excluding the water of composition; and that oxymuriatic acid consists of muriatic acid and oxygen, also excluding water of composition: or else on Sir H. Davy's hypothesis that oxymuriatic acid (chlorine) is a simple substance; that the dry muriats consist of the base, not oxydated, and of oxymuriatic acid; and that muriatic acid gas consists of oxymuriatic acid and hydrogen.

Therefore when water is produced by the union of muriatic acid gas and any *oxyd*, it may either be said that the water is simply expelled from the muriatic acid gas whilst uniting with the oxyd; or else that it is produced by the union of the oxygen of the oxyd with the hydrogen of the muriatic acid, whilst the base of the oxyd and the chlorine of the muriatic acid form the compound usually (but on this view incorrectly) termed a muriat. It would therefore be a decisive experiment as to the source of the water so produced, if it made its appearance when muriatic acid gas was united to some base that contained no oxygen, as in this case the water, or at least its oxygen, must of course proceed from the muriatic acid gas. Mr. Murray has therefore proposed as an *experimentum crucis* to combine dry muriatic gas with dry ammoniacal gas, since ammonia is not generally supposed to contain oxygen, and to examine carefully whether any water is condensed during the experiment.

This experiment has been performed apparently with great care, both by Mr. Murray who first proposed it, and by several other chemists, but with very differing results. We shall therefore not dwell upon the particulars at present. On the whole it appears that more difficulties than were at first supposed stand in the way of very accurate results. When the two gasses are mixed together, a very dense white cloud immediately appears, and if the gasses are pure and in proper proportions, they totally combine into a flocculent saline crust of muriat of ammonia. Some drops of water seldom fail to appear, but from the very volatile nature of the salt obtained, it is by no means easy to devise any unexceptionable mode of determining its actual dryness, or of expelling every particle of water that it may contain, with the same certainty that it may be expelled from the muriats of potash, of soda, or of any other fixed base. It must however be borne in mind, that the quantity of water thus produced should be considerable, in order to establish its source to be the muriatic acid gas, since this gas is inferred by all the experiments that are explained on this hypothesis to contain full one fourth of its weight of water.

**MURIATIC ACID.** The following estimation of the strength of solutions of muriatic acid gas in water of different specific gravities may be of practical utility.<sup>f</sup> The specific gravity of muriatic acid gas is to that of hydrogen nearly as 17 to 1. 100 cubic inches of it weigh at a mean temperature and pressure between 39 and

40 grains. Water at 40°. absorbs about 480 times its volume of the gas, and then forms a liquid muriatic acid of 1.2109 sp. gr., and 34.8 grains of muriatic acid gas dissolved in water and the solution precipitated by nitrat of silver will give about 132 grains of dry luna cornea, equal to 379.31 grains of luna cornea from 100 grains of muriatic acid gas.

At 45°. therm. and 30°. bar. 100 grains of liquid muriatic acid of 1.21 specific gravity contain about 42.42 grains of muriatic acid gas; and 100. grains of acid at 1.01 specific gravity contain 2.02 grains of acid gas. Hence in liquid muriatic acid at the above temperature and pressure, for every encrease of .01 specific gravity above unity, a corresponding encrease of 2.02 grains of muriatic acid gas in 100 grains of the liquid acid may be allowed, if the above data are accurate. Thus for example, 100. grains of liquid acid at 1.15 specific gravity, will contain  $2.02 \times 15 = 30.3$  grains of muriatic acid gas: and 2.02 grains of the acid gas will produce 7.662 grains of dry luna cornea.

We shall conclude this article with a short account of some further experiments undertaken by Dr. Henry, on the action of electricity on muriatic acid gas.<sup>g</sup>

The general accuracy of the former experiments is amply confirmed by the present series, but some slight corrections are required.

Dr. H. finds on the most careful examination, that under equal circumstances, precisely the same relative proportion of hydrogen gas is obtained from muriatic acid gas, whether it is or is not exposed to muriat of lime, which would shew that the latter gas is absolutely free from all hygrometric moisture.

The changes produced by electrifying muriatic acid gas *over mercury*, are a contraction of the volume of the gas, the formation of calomel and the evolution of hydrogen. But there is a natural limit to the decomposition of the same portion of gas by electricity, for by continuing the shocks, the action gradually diminishes, and after a time entirely ceases, though much of the muriatic acid gas remains undecomposed.

On the other hand, when muriatic acid gas is electrified in a close vessel, and not in contact with mercury, the same partial decomposition goes on, and hydrogen and oxymuriatic acid gas are produced, but as no mercury is in contact with the gasses, the oxymuriatic acid remains in the gaseous state, and therefore no diminution of bulk in the electrified gasses takes place.

<sup>f</sup> Phil. Trans. for 1812.

<sup>g</sup> Phil. Trans.

No water is condensed in either case. After an experiment of this kind, Dr. H. found on admitting water to the vessel containing the electrified gasses, and thus absorbing the unchanged muriatic acid gas, that the residue consisted of 100. measures of oxymuriatic gas, and 140 of hydrogen. These proportions widely differ from those that might be expected, from the fact that oxymuriatic acid and hydrogen unite in equal volumes to form muriatic acid gas; but the author shews that some of the deficiency in the oxymuriatic acid gas may be accounted for by being absorbed by the water employed to remove the muriatic acid gas. In making the experiment in a closed vessel, the greatest proportion of hydrogen obtainable by any continuance of the electrization, amounted only to about  $\frac{1}{7}$ th of the muriatic gas employed; while by electrization over mercury, from  $\frac{1}{4}$  to  $\frac{1}{8}$  of hydrogen was generally evolved. The author supposes this difference to arise from the circumstance of the mercury, when in contact with the electrified gas, removing the oxymuriatic acid as fast as it is formed, and in fact none of this acid is found in any other form than united with the mercury as calomel. Upon any theory of the constitution of muriatic acid, (Dr. H. observes) it may be expected that when in a mixture of that acid gas with hydrogen and oxymuriatic gasses confined in a close vessel, the two latter come to bear a certain proportion to the former, they will be brought within the sphere of mutual agency, and will reproduce muriatic acid. This point appears to be attained when the hydrogen and oxymuriatic acid taken together have the proportion to the muriatic acid of

about 1 to 35. Beyond this point the evolved gasses appear to re-act on each other, and reproduce muriatic acid gas, so that no further products of the decomposition of the muriatic acid are obtained by any continuance of the electrization on the same materials.

But where the oxymuriatic gas is removed by the contact of mercury as fast as it is formed, this cause of the limitation of the action of electricity does not exist. The cause is suggested by Mr. Dalton to be the presence of hydrogen alone; and in consequence Dr. Henry mixed 30 measures of hydrogen with 400 of muriatic acid gas, and passed 900 electric discharges through the mixture without the least apparent effect, none of the mercury with which the gas was confined being changed into calomel, and the hydrogen and muriatic acid gas being recovered unaltered after the end of the process.

When muriatic acid gas and oxygen are electrified together in a close vessel, water is deposited in drops on the inner surface of the vessel, in the form of liquid muriatic acid, owing to its union with a portion of this acid gas. When the stop-cock of the vessel is opened under mercury, a quantity of this metal rushes in, and has its surface instantly tarnished by the oxymuriatic acid generated. Indeed the production of this latter acid takes place merely by letting muriatic acid gas and oxygen remain together for some time over mercury; the volume of the gasses contracts, and calomel is formed on the surface of the metal.

All these facts are equally to be explained by either theory of the constitution of muriatic acid.

## N

NADELERZ. See BISMUTH.

NEPHELINE, H. Sommite, K.

The colour of this mineral is semitransparent greyish-white. It occurs usually in small hexahedral prisms either regular or replaced on the lateral edges, sometimes also in disseminated grains. The lateral edges are smooth and shining with a vitreous lustre. The longitudinal fracture is more or less foliated; the cross fracture is conchoidal. Its hardness is about equal to that of glass. Sp. gr. 3.27.

By the long continued action of the blowpipe it melts into a compact glass. A semitransparent fragment being digested in cold nitric acid acquires a nebulous opacity. It is composed, according to Vauquelin, of

46. Silix  
40. Alumine  
2. Lime  
1. Oxyd of iron

98.  
2. loss

It has hitherto been only met with lining the cells of certain lavas of Monte Somma, and is usually accompanied by Idocrase.

NICKEL.

A very long and minute account of this metal in a variety of its combinations has been published by M. Tupputi,<sup>a</sup> being the result of experiments made under the eye of M. Vauquelin,

<sup>a</sup> An. Ch. lxxviii. p. 133. lxxix. p. 153.

and with the assistance of this eminent chemist. Some particulars of M. Tupputi's valuable memoir may be here given.

*Pure Nickel.* This was obtained from *Speiss*, a compound residue of the Saxon ores of cobalt and nickel, containing sulphur, much arsenic, iron, copper, cobalt, nickel and a little manganese.

The ore was first dissolved in hot dilute nitric acid, and the solution evaporated considerably, by which most of the oxyd of arsenic was separated on cooling in the form of white crystals. The clear hot liquor was then slowly saturated with carbonat of soda, which first separated a yellowish-white arseniat of iron, followed by a rose-coloured precipitate of arseniat of cobalt and some nickel, which was succeeded by a pale green arseniat of nickel. When this began to appear, no further alkali was added, but the liquor (still acidulous) was diluted and a current of sulphuretted hydrogen gas was passed through, which after some time separated the arsenic in the form of yellow sulphuret. The clear liquor, which now contained only nitrat of nickel and excess of nitric acid, was decomposed by an alkali, and the pure oxyd of nickel was washed and dried.

This oxyd was then mixed with about 3 per cent. of pitch and reduced in a crucible lined with charcoal exactly in the same way as the reduction of the oxyd of manganese is accomplished, and with an equal intensity of heat.

The button of metallic nickel is of a colour between silver-white and steel-grey, sp. gr. 8.38 increasing to 8.82 after being forged, and scarcely less magnetic than iron. It is very considerably ductile and malleable, though it contains a little charcoal, which appears when the pure metallic part is dissolved by an acid.

*Oxyds and Hydrats.* 100 parts of nickel dissolved in nitric or muriatic acid, precipitated by a fixed alkali and calcined, give 127 parts of a blackish ash-grey insipid oxyd. This is the base of most of the salts of nickel in acids, and is the *suboxyd* of nickel.

The *Peroxyd* of nickel, first discovered by Thenard, is easily prepared by passing oxy-muriatic gas through the suboxyd when just precipitated and diffused in water; or by shaking the wet hydrat of nickel with a solution of oxy-muriat of lime. This peroxyd is black, and gives out oxygen when it dissolves in sulphuric, nitric, or muriatic acids.

When a pure alkali is added to the salts of nickel, or when the solution of carbonat of

nickel in ammonia is heated, a greenish white bulky granular *Hydrat* of nickel is separated, 100 parts of which lose 24 of water by low ignition, leaving 76 of the suboxyd.

*Sulphuret of Nickel* is easily formed by melting sulphur with metallic nickel or with the dry oxyd. It is brass-yellow, soluble in acids, and unmagnetic.

Nickel is not separated in its metallic state from its solutions by the addition of any other metal. Zinc alone troubles these solutions, and precipitates a little oxyd of nickel when there is no excess of acid; but when there is, a soluble triple salt of nickel, zinc, and the acid employed is produced, and the liquid remains clear.

*Sulphat of Nickel.* Sulphuric acid, when concentrated, hardly acts upon metallic nickel, but when diluted dissolves it with great ease, giving out much hydrogen and leaving untouched the small portion of carbon which the metal always contains. This solution forms green crystals of sulphat of nickel of the form of a rectangular prism, of a sweet and astringent taste, soluble in thrice its weight of cold water, and efflorescent when kept in the open air. A hundred parts of this salt lose in a red heat 55 parts of water along with a little acid, so that the calcined residue gives a blue to litmus. The oxyd of nickel in 100 of the crystallized salt is 25.63, leaving 29.37 for the acid.

*Nitrat of Nickel.* Nitric acid of any degree of strength dissolves nickel with ease, giving out much nitrous gas. The crystals of the salt are octagonal prisms, blueish-green, soluble in two parts of cold water and also in alcohol. When heated to redness it becomes yellow and olive coloured, loses acid, and is then a nitrat with excess of base, or a *subnitrat*. By continuing the heat the pure oxyd alone is left.

*Muriat of Nickel.* This metal dissolves readily in muriatic acid, forming when concentrated a confusedly crystallized mass of an apple green colour, soluble in less than twice its weight of water and also in alcohol. This last solution burns with a pale blue flame, passing to green as it becomes concentrated.

*Phosphat of Nickel.* The phosphoric acid when dilute dissolves nickel with ease, but this phosphat being insoluble, it is difficult to saturate the acid in this manner. The phosphat is made with perfect ease by any of the soluble salts of this metal and the phosphat of soda. Phosphat of nickel is green, nearly insipid, soluble in an excess of its own or of many other acids, but not in water.



*Borat, Carbonat, Arseniat of Nickel.* These salts are best formed by double decomposition. They are insoluble in water.

*Chromat of Nickel.* The chromic acid alone forms with the hydrat or wet carbonat of nickel a yellowish red solution, which however does not crystallize. Nitrat of silver added to it gives large red flocculi of chromat of silver. The alkalies all produce a yellowish red precipitate, probably a mixture of the oxyds of chrome and nickel.

Nickel has a peculiar tendency to form triple salts, so that a *sulphat of potash and nickel* is readily formed by evaporating a mixture of the two sulphats, and in like manner a *sulphat of ammonia and nickel*, a *sulphat of zinc and nickel*, and other triple salts may be produced.

*Nickel and Ammonia.* The hydrat of nickel dissolves with ease in liquid ammonia. The liquid is at first violet, but passes to a deep blue in proportion as the alkali becomes saturated. This solution when exposed to the air lets fall green flocculi, which are the triple *carbonat of ammonia and nickel*, as Proust first observed. The colour of the ammoniacal solutions of nickel is blue, but that of the neutral salts of nickel is green, and as most of the soluble salts of this metal contain a slight excess of acid and strongly tend to form triple combinations, the addition of ammonia to them does not at first disturb the green colour, but the blue begins to prevail when this alkali is in excess.

*Sulphuretted Hydrogen*, either gaseous or liquid, has but little action on the solutions of nickel in the mineral acids. A current of this gas passed through the liquid hardly renders it turbid. But on the other hand if the acid is vegetable, (the acetite of nickel for example) the solution is rapidly and almost entirely precipitated by the gas, leaving the clear liquor nearly colourless.

The author gives the following rules for determining the purity of metallic nickel.

It should dissolve totally in muriatic acid, except the small alloy of carbon which it has acquired during its reduction.

The solution, after the excess of acid has been driven off by heat, should give a yellow stain to paper when heated.

Prussiat of potash should give a yellowish white precipitate passing to green, and this should dissolve totally in ammonia into a dusky rose-coloured liquid, copiously depositing shining crystalline plates of a dun red colour when viewed by refracted light. When the

ammoniacal solution is supersaturated with an acid, the liquor should not be troubled either by iron or by sulphuretted hydrogen, or by a further addition of ammonia; only this latter alkali, when it predominates, will give the whole a blue colour.

The muriatic solution when diluted with water should give white flocculi on adding tincture of galls, which are directly redissolved by an excess of the precipitant; but on adding much ammonia, a copious dun yellow precipitate will appear.

The metals with which nickel is usually alloyed are iron, copper, cobalt, bismuth and arsenic.

Iron will be detected by a blueish green precipitate insoluble in ammonia on adding prussiat of potash; or by a fine purple one on adding an excess of ammonia, followed by tincture of galls.

Copper will be shewn by a peach-flower precipitate on adding prussiat of potash, which is totally soluble in ammonia.

Cobalt is distinguished by forming a green sympathetic ink when heated.

Bismuth will be immediately blackened by sulphuretted hydrogen gas.

Arsenic will be deposited as a yellow hydro-sulphuret by the same reagent.

To this account of some of the leading properties of pure nickel we may add some particulars on a very difficult problem in analytical chemistry, the compleat separation of cobalt from nickel contained in the same solution. These experiments are given by Hisinger and Murray,<sup>b</sup> in an examination of a supposed new metal, *Niccolanum*, announced by Richter, but which appears to be an alloy of nickel, cobalt and iron.

The presence of cobalt with nickel being suspected, Thenard's method of separating them by first bringing them to a high degree of oxidation and then adding ammonia was tried. The nitric solution of the mixed metals was exactly saturated with caustic potash and the blue-green precipitate, while still wet, was shaken in a phial containing a solution of oxymuriat of lime. This blackened the precipitate, which was then well washed to separate all adhering oxymuriat of lime, and was afterwards thrown into caustic ammonia. A deep blue solution, without any mixture of red or garnet tinge was formed, and after digestion for some days, the blue liquid was poured off from the undissolved oxyd. The liquid evaporated to

<sup>b</sup> Annals of Philosophy, No. 2.

dryness left a green oxyd, black when ignited, which dissolved before the blowpipe in phosphat of soda into a bead, blood-red when hot, but honey-yellow when cold, which was pure oxyd of nickel. So far the process answered well, but the oxyd remaining undissolved by the first portion of ammonia, now gave a *reddish* blue solution with fresh ammonia, which was found by further examination to be owing to the presence of a portion of cobalt along with the nickel.

It therefore appears probable that the per-oxyd of cobalt loses oxygen by digestion in ammonia, and *then* becomes soluble in some degree in this alkali.

The method of separating these two oxyds which these chemists adhere to is that of Proust, namely, to saturate the mixed ammoniacal solution with sulphuric acid, and by careful evaporation to obtain deep green crystals of sulphat of ammonia and nickel, while the sulphat of cobalt is left as a confused mass of a rose red colour. The green crystals may then be picked out from the red salt, and each decomposed separately.

NITRIC ACID, &c. }  
 NITROUS GAS. } See AZOTE.  
 NITROUS OXYD. }

## O

## OIL. FIXED.

It is generally asserted that the fixed oils are insoluble in alcohol in their natural state, but as we have mentioned under the articles OIL and SOAP (Chem. Dict.), when a fixed oil has first been chemically united to acids or to alkalies, and then separated by substances that have a stronger affinity to them, it becomes so much altered as to be often abundantly soluble in alcohol, and also in ether. But it has been found by careful experiments that all the fixed oils, even in their natural state, are in some slight degree soluble in highly rectified alcohol, and one of them, viz. castor oil, dissolves in this liquid in great abundance. This was first noticed by Rose, and afterwards by Bucholz.<sup>a</sup> Castor oil mixes with highly rectified alcohol in every proportion. Oil of almonds requires for solution about 30 parts of alcohol; linseed oil 20 parts; poppyseed oil 30 parts, &c.

Mr. Brande in his examination of a vegetable wax lately imported from Brazil, has the following observations on the solubility of the fixed oils in alcohol and ether.<sup>b</sup>

Four fluid ounces of sulphuric ether of .7563 sp. gr. dissolved  $1\frac{1}{4}$  fluid oz. of oil of almonds,  $1\frac{1}{2}$  oz. of olive oil,  $2\frac{1}{2}$  oz. of linseed oil, and mixes uniformly with any proportion of castor oil.

Four fluid ounces of alcohol of .820 sp. gr. dissolve 1 fluid dram of linseed oil; and mix uniformly with any proportion of castor oil. But the action of alcohol on these oils is extremely lessened when the spirit is diluted, so that common spirit of wine has but little action even on castor oil. Camphor which so much

assists the solubility of some of the resins in alcohol, has a similar effect on castor oil, which is abundantly soluble in spirit of .840 sp. gr. when previously combined with an eighth part of camphor. The other fixed oils however are not rendered more soluble by this means.

Water separates all these oils from their alcoholic solution, first making a milky liquor, after which the oil gradually collects on the surface in its original state.

With regard to the oil separated from soap by an acid, Mr. Haussman asserts that it thus acquires the power of acting upon bitumen, asphaltum and copal.<sup>c</sup>

## OIL ESSENTIAL.

For some further experiments on the relation of essential oil with camphor, see CAMPHOR.

OLEFIANT GAS. See CARBURETTED HYDROGEN.

OSMAZOME. See BRAIN.

OXALIC ACID. OXALATS.

We have to notice some very interesting experiments on the composition of this acid and of its compounds. Those of Dr. Thomson<sup>d</sup> are peculiarly so, both from the skill and pains shewn in the analysis itself, and from the happy illustration of the Daltonian system which he has deduced from the composition of this acid. Part of this subject, together with Dr. Wollaston's additions, have been already noticed in the article *Affinity*, of this Appendix. The practical part and the general results remain to be mentioned.

The quantity of water of crystallization in oxalic acid was found by first adding to a solution of muriat of lime so much of a solution

<sup>a</sup> Ann. Chim. tom 69.

<sup>b</sup> Phil. Trans. for 1811. p. 265.

<sup>c</sup> Ann. Chim. tom. 58. p 185.

<sup>d</sup> Phil. Trans. for 1803

of crystallized oxalic acid as exactly separated the whole of the lime; then drying the oxalat of lime on a sand-bath at a heat between 200° and 300°; and then calcining the oxalat in an open platina crucible till nothing but pure lime remained. This gave the composition of the oxalat of lime, and hence the quantity of oxalic acid used in its production, and hence the difference of weight between the real or dry oxalic acid in the oxalat and in the crystallized acid employed, or in other words, the water of crystallization. In precipitating the lime from the muriatic solution by the oxalic acid it is necessary from time to time to saturate the excess of free muriatic acid in the supernatant liquor, which otherwise would dissolve part of the oxalat of lime and vitiate the result.

Exactly the same composition of oxalat of lime as that found in this manner was obtained by the direct combination of oxalic acid and lime-water. In both the dried salt consisted of 62.5 of acid, and 37.5 of lime.

The composition of the oxalats of the alkalis and of the alkaline earths was ascertained (with all except magnesia) by the direct union of the acid and base, always estimating the proportion of water of crystallization in the acid as the same with that found by means of the dry oxalat of lime. These oxalats were dried in the same manner, and it was inferred that little or no water of crystallization adhered to any of these salts after drying, except to the oxalat of potash, which Dr. T. conjectures to retain as much as 10 per cent. The oxalat of magnesia, on account of the great insolubility of this earth, was formed by the addition of oxalat of ammonia to sulphat of magnesia. It is remarkable that though the oxalat of magnesia is apparently equally insoluble in water as oxalat of lime, no turbidness appears on adding oxalat of ammonia and sulphat of magnesia till the liquor is much reduced in bulk or heated, or till they have stood together for some hours. When the oxalat of magnesia is once obtained, in either of these ways, or else by entire evaporation of the mixture and adding water to dissolve out the sulphat of ammonia, it is a tasteless insoluble powder.

Oxalat of ammonia crystallizes in long prisms. It requires more than 20 parts of cold water for its solution.

The exact composition of these oxalats we shall give presently, as well as the result of the author's experiments on the ultimate analysis of oxalic acid.

The composition of the oxalats and superoxalats has also been examined by Mr. Berard,\* the results of which have a tolerable agreement with those of Dr. Thomson, though with some considerable deviations. M. Berard has also more particularly examined the superoxalats which are but little noticed by Dr. T.

M. Berard also takes the composition of the dry oxalat of lime as the basis of his calculations, and he gives almost exactly the same proportions in this salt as Dr. T. does, namely, 62 per cent. of acid, and 38 of lime. He also finds that the acid which sublimes unchanged in the dry distillation of crystallized oxalic acid is oxalic acid nearly as free from water of crystallization as it exists in the dried oxalat of lime.

We shall not enter into all the particulars of these experiments, but shall give the results. The crystallized oxalic acid employed for combination with the several bases contained 27.3 per cent. of water: that of Dr. Thomson contained 23. per cent. but as the composition of the dry oxalat of lime was nearly the same in each, this difference in the acid does not affect the result.

	Acid.	Base according to Dr. Thomson	Base according to Berard
Oxalat of Ammonia	100.	34.12	38.2
— Magnesia	100.	35.71	37.6
— Soda - -	100.	57.14	69.7
— Lime - -	100.	60.00	61.2
— Potash -	100.	122.86	102.7
— Strontian	100.	151.51	119.5
— Barytes -	100.	142.86	164.3

The composition of the superoxalats was as follows in M. Berard's experiments, compared with the corresponding neutral oxalats:

*Superoxalat of Potash* was formed by crystallizing a mixture of the neutral oxalat of potash with an excess of acid. It is less soluble than the neutral salt. Ten parts gave by ignition 4.910 of fused carbonat of potash, of which the alkali was 3.46: and ten other parts of the same superoxalat decomposed by muriat of lime gave 10.6 of oxalat of lime, containing 6.58 of oxalic acid. Hence this superoxalat contains 65.8 of acid, and 34.2 of base.

*Quadroxalat of Potash.* This salt, discovered by Dr. Wollaston, may be formed either by adding more oxalic acid to the superoxalat, or by boiling a solution of muriat of potash with oxalic acid. This quadroxalat is less soluble than the two other salts of oxalic

\* Ann. Chim. tom. 73.

acid and potash. Analyzed in the way above-mentioned it gave

18.95	Potash
72.05	Oxalic Acid
9.00	Water
<hr/>	
100.00	

Hence the respective quantities of oxalic acid saturating 100 parts of potash in these three oxalats are,

In the neutral oxalat of potash	97.6
In the superoxalat	192.
In the quadroxalat	381.

which numbers are nearly in the rates of 1, 2, and 4.

The superoxalat is known more commonly as the *Salt of Sorrel*, and is used under this name in many parts of Europe. M. Berard mentions, that sometimes the quadroxalat is met with as salt of sorrel of the shops.

The *Oxalat of Soda* is but little soluble in water, and contains 143.3 of oxalic acid to 100 of soda.

The *Superoxalat of Soda* contains 284.7 of acid to 100 of soda, which is almost exactly thrice the quantity of that in the oxalat. This superoxalat is still less soluble in water than the oxalat, and may be formed either by the direct combination of the oxalat and oxalic acid, or by the action of oxalic acid on muriat of soda. The author could not produce any quadroxalat.

*Oxalat of Ammonia.* The composition of this was determined by saturating oxalic acid with liquid ammonia, which, according to Berthollet, at .9656 specific gravity, contains 8.761 per cent. of pure ammonia. The *Superoxalat of Ammonia* contained nearly a double proportion of acid.

Both an *Oxalat of Barytes* and a *Superoxalat of Barytes* exists; in the former of which 100 of barytes combine with 60.84 of oxalic acid; and in the latter with 123. of the same acid. This superoxalat is formed by boiling muriat of barytes with oxalic acid, which deposits the superoxalat in crystals on cooling. This compound is decomposed by mere boiling with water, which abstracts the excess of acid and reduces it to the simple oxalat.

The author has found no *Superoxalat of Strontian*, and the composition of the oxalat is given differently from that of Dr. Thomson, as will be seen by the table. M. Berard states that the oxalat of strontian which separates

from the muriat of strontian with neutral oxalat of ammonia, is very little soluble, and the supernatant liquor remains equally neutral as before, which is a proof that the oxalat of strontian is itself neutral.

*Ultimate Analysis of the Oxalic Acid.* This was performed by Dr. Thomson, by the destructive distillation of perfectly dry oxalat of lime, and by analyzing all the gaseous products. The particulars of this analysis we shall not give, as the general mode, together with the difficulties that oppose a very accurate result, have been described under the article *Carburetted Hydrogen*. The general result is, that dry oxalic acid consists of

Oxygen	-	64
Hydrogen	-	4
Carbon	-	22
		<hr/>
		100.

taking this in round numbers.

Professor Berzelius gives the composition of oxalic acid somewhat differently<sup>f</sup> as to the proportion of hydrogen, being 35.02 of carbon, 0.68 of hydrogen, and 64.30 of oxygen. But the dry oxalat from which he formed his calculation was that of lead, which appears to have retained a much less proportion of the oxalic acid than the lime, since Professor B. reckons the crystallized acid to contain as much as 42 parts per cent. of water of crystallization; or, in other words, when 100 parts of the acid are boiled and evaporated to dryness along with pure oxyd of lead, the latter receives from the acid an addition of only 58 parts.

Lastly, the composition of oxalic acid is estimated by Gay Lussac and Thenard, by means of deflagration with oxymuriat of potash, to consist of

Oxygen	-	70.69
Hydrogen	-	2.74
Carbon	-	26.57

which, supposing all the hydrogen to take as much oxygen as would convert it into water, would make, instead of the above quantities of these two substances, 22.87 of water, and 50.56 of oxygen in excess. These chemists employed the dry oxalat of lime as the form in which the dry oxalic acid may be exhibited, and they give the composition of this salt to be 61.345 of acid, and 38.655 of lime, which agrees very closely with the numbers given for this salt, both by Dr. Thomson and M. Berard. (See the article *ANALYSIS Vegetable and Animal*, in this Appendix).

<sup>f</sup> Ann. Chim. tom. 81, p. 300.

**OXYCARBURETTED HYDROGEN.**  
See CARBURETTED HYDROGEN.

**OXYMURIATIC ACID.** See MURIATIC ACID.

## P

**PARANTHINE.** H. Scapolite. K.

The primitive form of this mineral appears to be a strait prism with square bases. The general figure, however, of its crystals, is an eight-sided prism terminated by planes or by tetrahedral pyramids. In some varieties the crystals are cylindrical, deeply striated longitudinally and laterally aggregated into bundles or plates. Sometimes also it occurs amorphous. Its colour is ash-grey, greenish, yellowish or brownish. When transparent, its lustre is

Vitreous
45. Silix
33. Alumine
17.6 Lime
1. Iron and Manganese
1.5 Soda
0.5 Potash

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98.6

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vitreous, but by the progress of decomposition it becomes translucent, with a semi-metallic or pearly lustre. When perfect it scratches glass. Its longitudinal fracture is imperfectly conchoidal. Sp. gr. 3.6—3.7.

Before the blowpipe it melts with intumescence into a brilliant white enamel. The vitreous variety has been analyzed by Laugier, and the pearly by M. Simon, with the following results.

Pearly
53. Silix
15. Alumine
13.25 Lime
7. Manganese
4.5 Oxyd of Manganese
2. Oxyd of Iron
3.5 Soda

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98.25

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It has hitherto been met with only near Arendahl in Norway, in the iron mines, mixed with mica, calcareous spar, and felspar.

**PHOSGENE GAS.** See MURIATIC ACID.

**PHOSPHORUS.** PHOSPHORIC ACID. PHOSPHATES, &c.

Messrs. Fourcroy and Vauquelin, in their analysis of Fish Roe (Ann. Chim. tom. 64) announced the discovery of phosphorus existing in this substance uncombined with any base, and obtained by simple distillation of the roe, which in its natural state could contain no free phosphoric acid nor phosphat of ammonia. The editor of this journal adds, that this discovery of free phosphorus in organized bodies is entirely due to these chemists, as the only parallel case is the assertion of Margraaf, that he obtained phosphorus by the simple distillation of mustard seed, to which the editor is inclined to give little credit.

But M. Theodore de Saussure<sup>a</sup> has given some experiments which appear both to confirm the accuracy of Margraaf, as to the fact of obtaining phosphorus from seeds, and to throw doubts as to the real source of this phosphorus. He observes, that some years ago he had been

strongly heating the black ashes of burnt beans, in a platina crucible, and he found part of the ash strongly agglutinated to the vessel, which was perforated and melted down in that place. A similar accident happening to Messrs. F. and V. in their analysis of fish-roe, they rightly attributed it to the action of phosphorus on the platina vessel, which caused M. T. de Saussure to undertake the distillation of wheat with care. Some wheat was first heated by itself for three hours moderately red-hot in an earthen retort, till no more vapours appeared. The coaly residue was then transferred to a small coated porcelain retort, fitted to a tubulated receiver, half full of water, and heated most intensely for three hours, in a fire strong enough to vitrify the lute entirely. A white fume smelling like phosphorus appeared at the end of the process, and the tube connecting the retort and receiver was found lined with a film of perfect phosphorus.

As the coal of wheat which furnished this phosphorus is sensibly alkaline, it is obvious that the phosphorus cannot proceed from any free phosphoric acid; neither is it likely that the previous calcination should have allowed

any phosphat of ammonia to remain in the coal. There is only therefore the phosphat of potash and phosphat of lime which could furnish the phosphorus; but as these salts have usually been thought undecomposable by charcoal, the author made the experiment.

Thirty grammes of pure phosphat of potash, with a little excess of alkali, were mixed with twice as much beech charcoal, previously heated red-hot. The whole was intensely heated in a porcelain retort for four hours, and at the end about  $2\frac{1}{2}$  grammes of phosphorus were collected, besides what was carried off in a gaseous form as phosphuretted hydrogen, and the oxyd of phosphorus which remained suspended in the water of the receiver. As the 30 grammes of phosphat of potash only contain by calculation 4.8 grammes of phosphorus, it cannot be doubted that phosphat of potash is decomposable by charcoal, and yields pure phosphorus.

Phosphat of soda treated in the same manner yielded the same proportion of phosphorus.

Phosphat of lime was prepared by adding phosphoric acid to nitrat of lime and separating the phosphat of lime by ammonia. Ten grammes of this phosphat previously made red-hot, were mixed with twice as much beech charcoal, previously washed to separate the small portion of alkaline and saline matter. This was heated in a porcelain retort as before, but the results were not so decided as in the last experiments, owing, as the author supposes, to the heat not being sufficiently intense. A similar mixture was therefore enclosed in a Hessian crucible, with a cover of platina, and the whole was imbedded in charcoal powder, in an outer earthen crucible and cover. This was heated two hours as intensely as possible. When cold, the platina cover was found melted, but the earthen crucible was sound. The contents that remained were digested in muriatic acid, and then precipitated, first by ammonia, which separated 4.52 grains of phosphat of lime, and then by carbonat of ammonia, which separated 5.22 grains of carbonat of lime. Hence it appears that about half the phosphat of lime had been decomposed in the process of ignition with charcoal. The phosphorus had of course been lost and consumed in the open fire, into which it had escaped.

The same experiment was repeated with the native Spanish phosphat of lime. Less of it was decomposed, but enough to render the experiment quite satisfactory.

It appears therefore, that it is a mistake to

suppose that the phosphats of potash, soda, and lime, are undecomposable by heating with charcoal, and that former experiments have failed probably from not having the heat intense enough, or continuing it long enough.

It also appears as a direct inference from these experiments, that some traces of phosphorus, either in substance or as phosphuretted hydrogen, must be obtainable from all animal and vegetable matters by simple distillation, since they all contain phosphat of lime and charcoal: and hence that the appearance of phosphorus in these experiments is not of itself a sufficient mark of uncombined phosphorus in the substance distilled.

#### *Phosphuretted Hydrogen.*

It was mentioned under the article *Phosphorus* (*Chem. Dict. vol. 2*) that there appeared to be two distinct combinations of phosphorus and hydrogen, one is the well-known phosphuretted hydrogen, formed by heating phosphorus in a liquid solution of potash, and which is spontaneously inflammable when in contact with the air: the other is a gas which is a compound of phosphorus and hydrogen, but does not inflame spontaneously, and is probably the same as that produced by merely confining phosphorus in hydrogen. The properties of this gas, hitherto but little known, have been more fully investigated of late.

M. Theodore de Grotthuss, in a memoir on the metallic phosphurets notices a peculiar gas,<sup>b</sup> produced by boiling together liquid potash, phosphorus, and alcohol, which has the scent of phosphuretted hydrogen, but does not inflame spontaneously when mixed with oxygen, though the mixture detonates strongly when touched by any ignited body, and white phosphoric vapours concrete on the vessel. This gas detonates still more intensely and dangerously when mixed both with nitrous gas and oxygen, and ignited. With oxymuriatic gas it burns spontaneously and without explosion, with a beautiful green light. The products of the combustion are phosphoric acid, water, and carbonic acid. This compound gas therefore seems very distinct from the *sub-phosphuretted hydrogen* in question.

But this sub-phosphuret is more unequivocally noticed and its leading properties described, by Messrs. La Grange and Vogel, in a memoir on the action of phosphorus on alkalies.<sup>c</sup> The following is the experiment: melt some phosphorus in a phial full of hot water, cork it, and shake it violently till the water is cold,

<sup>b</sup> Ann. Chim. tom. 64, Oct. 1807.

<sup>c</sup> Ib. 66. for 1808.

by which means the phosphorus will be simply divided into a fine powder. Dry this on blotting paper, mix it hastily with some dry caustic potash, just reduced to powder in a brass mortar cooled by ice, and put the mixture into a small luted earthen retort, with a tube of safety and a conducting tube to a mercurial trough. Heat the retort at first gently, and then gradually increasing to whiteness. During the whole time a peculiar gas arises, which has the following properties: it is neither acid nor alkaline; it has a slightly alliaceous smell; it burns on the approach of a taper, but not spontaneously, either in oxygen or nitrous gas: when mixed with oxygen and ignited it detonates strongly: it is a little soluble in water, and the solution gives a black precipitate with nitrat of silver: it inflames rapidly with oxymuriatic gas, and then deposits some oxyd of phosphorus on the vessel. The residue of this distillation is a black shining mass resembling plumbago. It may be added, that where the only object is to procure the gas, and not to examine the action of phosphorus with accuracy, nothing more is required than to put a few small bits of phosphorus in a glass bottle, to cover them with very dry caustic potash, to adapt a tube going to a mercury bath, and to heat the bottle moderately, when the gas will be given out in abundance. If the alkali is wet, the gas will be the common spontaneously inflammable phosphuretted hydrogen, but by continuing the heat till the visible moisture is expelled, the above less inflammable gas succeeds. As later researches have shewn that even the fused dry caustic alkalies contain much water in their composition, there can be no difficulty in finding the source of the hydrogen on heating phosphorus and dry alkali.

This same sub-phosphuretted hydrogen (as it appears to be) has been also examined by Sir H. Davy with more accuracy, as to the proportions of its composition, and it has received from him the name of *Hydrophosphoric Gas*. It was obtained by heating in a close vessel solid *hydrat of phosphorous acid* (which will be presently described). Solid phosphoric acid is formed and a large quantity of this gas is given out apparently of great purity. This gas has all the properties of that just described, that is, in not being spontaneously inflammable, but exploding violently when mixed with oxygen, and exploding in oxymuriatic gas without the contact of an ignited body. Water absorbs

one-eighth of its volume of this gas. The specific gravity of the gas is about 87 (common air being 100.) or 12 times that of pure hydrogen.

When potassium is heated in this gas, its volume is doubled, the phosphorus is extracted by the potassium, and pure hydrogen remains. Sulphur sublimed in it also doubles the volume, phosphuretted sulphur is produced, and the remaining gas is phosphuretted hydrogen. It appears to consist of 4.5 by weight of hydrogen, to 22.5 of phosphorus.

On the other hand, the common inflammable phosphuretted hydrogen has much less specific gravity, and never enlarges to more than 1.5 of its bulk of pure hydrogen when the phosphorus is extracted by potassium, and probably contains a double proportion of phosphorus.

Two distinct combinations of phosphorus and oxygen were described (*Ch. Dict. Art. Phosphoric Acid*) the *Phosphoreous* and *Phosphoric Acids*. Sir H. Davy gives the following estimation of their composition.<sup>d</sup> When phosphorus is heated in highly rarefied air three products are formed, one of them is *Phosphoric Acid*, which is fixed; another is a white powder, easily volatile, with a sour taste and garlic smell, and which burns when heated strongly, passing to the state of phosphoric acid. This volatile white powder is the *Phosphoreous Acid*, but mixed with a little phosphorus. The third substance is a red *Oxyd of Phosphorus*.

The phosphoreous acid is obtained in union with water by subliming phosphorus through corrosive sublimate (in the way described under the article *Muriatic Acid* in this Appendix) and mixing the limpid compound of chlorine and phosphorus with water, and evaporating the solution to the consistence of syrup. Muriatic acid is given out, and the residue is a compound of phosphoreous acid and water, called by the author *Hydrophosphoreous Acid*. This as above mentioned, yields one of the species of phosphuretted hydrogen when heated.

Phosphoreous acid consists of about 20 of phosphorus and 15 of oxygen.

Phosphoric acid consists of 20 of phosphorus and 30 of oxygen.

The composition of the red oxyd is not well ascertained.

M. Thenard<sup>e</sup> finds that phosphorus always contains carbon, however often it is rectified, but when the carbon is in small quantity it does not impair the colour of the phosphorus.

M. Thenard denies the existence of the supposed red oxyd of phosphorus, but considers it as a combination of phosphorus and carbon.

When the purest phosphorus is burned slowly in the air, some carbonic acid is obtained, owing to the combustion of the carbon which it contains. This amounts to 2 or 3 per cent. of the air employed, which, when phosphorus is employed eudiometrically, causes an error to this amount by making the absorption appear too little. This may be corrected by potash, which removes the carbonic acid. In the rapid combustion of phosphorus the carbonic acid is not produced.

PICROMEL. See BILE.

PINITE.

The primitive form of this mineral is a regular hexahedral prism, but it also occurs as a dodecahedral prism, and as a hexahedral prism with the lateral and terminal edges replaced by secondary facets. It is often quite opaque, sometimes slightly translucent; its colour is blackish grey often superficially tinged by oxide of iron. Its cross fracture is imperfectly foliated, its longitudinal fracture is small-grained, uneven, with a glistening resinous lustre. It yields easily to the knife. Sp. gr. 2.98.

It is infusible *per se* before the blowpipe.

It was first found in the mine called Pini, at Schneeberg in Saxony, and has since been met with in France. It occurs in crystals single or crossing each other, and accompanied by quartz, felspar, and mica.

The Saxon variety has been analyzed by Klapproth, and the French by M. Drappier, with the following results.

63.75	—	42	-	Alumine
29.5	—	46	-	Silex
6.75	—	2.5		Oxide of iron
		7.		Volatile matter

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100. — 97.5

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## PLATINA.

### § 1. Ores of.

Since the publication of the Chemical Dictionary, platina, which at that time was considered as the peculiar product of Peru, has been ascertained to occur in the island of St. Domingo, in Brazil and in Spain.

The platina of St. Domingo<sup>a</sup> is met with in the eastern part of that island, in the sands of a river called Jaki, at the foot of the mountains of Sibao. It is in the form of flattened grains somewhat larger than the Peruvian, and is

accompanied by magnetic iron ore, by gold, and probably by the other metallic substances which are mixed with the Peruvian ore: it has not as yet been analyzed.

The platina of Brazil<sup>b</sup> is found in the gold mines of that country in the form of small grains or fragments of a spongy texture, and entirely destitute of polish. It has been examined by Dr. Wollaston, and appears to be a natural alloy of this metal with gold and silver; and is mixed with grains of gold and of palladium alloyed with iridium, and probably with osmium and rhodium. It does not contain any of the magnetic iron sand or of the minute hyacinths which always accompany the Peruvian ore.

The Spanish platina was discovered by Vauquelin in an examination of the grey silver ore from the mines of Guadalcanal in Estremadura. This ore appears to contain copper, lead, antimony, iron, silver, sulphur, sometimes arsenic and platina, the proportion of which last varies from the smallest perceptible quantity to about 10 per cent. The gangue of this ore is generally calcareous spar, mixed with heavy spar and quartz.

The platina may be obtained from this ore by treating it alternately with nitric and muriatic acids, in which case the platina will remain undissolved together with the sulphur: or it may be procured by finely pulverizing and roasting the ore, then melting it with common potash into a metallic button, and afterwards submitting it to cupellation, being mixed on the cupel with the due proportion of lead if the quantity naturally contained in the ore is not sufficient. The result of this process will be a button composed of silver and platina, from which the former is to be separated by quartation as described in the article ASSAY.

### § 2. Analysis of Crude Platina.

Nearly about the same time that Mr. Tennant and Dr. Wollaston were engaged in their examinations of crude platina (the interesting and important results of which have already been detailed in the Chemical Dictionary, article PLATINA,) M. Descotils and M. M. Vauquelin and Fourcroy were also occupied on the same subject. Their success indeed has not been so absolute and satisfactory as that of the English chemists, yet it well worthy of notice as tending, as far as it goes, to illustrate and confirm the other discoveries.

M. Descotils<sup>c</sup> began his operations by separating the heavier from the lighter grains of

<sup>a</sup> Ann. Chim. lxxiii. p. 334.

<sup>b</sup> Phil. Trans. 1809, p. 189.

<sup>c</sup> Ann. Chim. xlvi. p. 143.



the crude platina, by means of a common bellows. The lighter part thus separated, consisted of siliceous grains of ferruginous sand attractable by the magnet, and of ferruginous sand not attractable. Of the two last the former proved to be menachanite, and the latter chromate of iron.

The heavier grains were put into a porcelain retort, to which was adapted a balloon one third full of water, an intense heat was applied for two hours, and during the whole of the time light vapours were given off of a sulphureous odour, and in part soluble in the water of the receiver. At the end of the process the colour of the fluid was pale greenish, and in the course of a few days it had changed to a full ultramarine blue. The platina in the retort was agglutinated; and in the upper part of the mass the grains were brownish, as if they had been rusted; at the bottom the grains were scarcely coherent, and had retained their original metallic lustre.

The blue liquor in the receiver was first examined. With alkalies it yielded a blue deposit. By nitric and oxymuriatic acids the colour was first changed to lilac, and at length was entirely destroyed. Sulphuretted hydrogen gave no precipitate; but hydro-sulphuret of ammonia threw down a grey precipitate, which was changed by acids to blue. A blue sublimate had adhered to the beak of the retort; of this a part was fused with borax, and in consequence the blue matter assumed a metallic appearance, the borax remaining colourless: another portion being heated *per se* before the blowpipe was volatilized.

The platina remaining in the retort was next submitted to examination. For this purpose it was first digested with muriatic acid, in order to separate the greatest part of the iron, and then was exposed to the action of nitro-muriatic acid: during the action of this menstruum a black powder made its appearance, which if separated from the solution in proportion as it formed, amounted to about 3 per cent. but if left in the acid was for the most part dissolved.

The solution after it had become clear by subsidence was poured off, and concentrated solution of muriate of ammonia was added as long as any turbidness took place; the precipitate was yellow and was carefully washed till the washings were no longer coloured green by prussiate of potash. The residual liquor and washings were now mixed, concentrated by evaporation and again treated by muriate of ammonia which now threw down a deep red precipitate.

The residual liquor was again evaporated and subjected to the same treatment as before, by which a second very red precipitate was obtained.

The black powder was next digested in nitro-muriatic acid, in which it was found to be partially and with difficulty soluble. The solution of a dark redish brown colour, afforded with muriate of ammonia, a precipitate apparently the same as the second red precipitate procured from the solution of the platina.

Equal quantities of the yellow salt obtained from the first precipitation and of the red salt obtained from the second precipitation were dissolved in equal portions of water. The colour of the former was bright golden yellow, that of the latter was redish-yellow with a tinge of green. Sulphureous acid or green sulphate of iron immediately, and alcohol after a time brought the latter solution to the same colour as the former. This circumstance induced M. D. to suppose that the deeper tinge of the one was owing to its being in a state of higher oxydation than the other. In consequence the yellow solution was treated with nitric acid, but without bringing it to the same degree of intensity of colour as was possessed by the red solution. Oxymuriatic acid was then tried, but the effect of this was to decompose the ammonia, and thus bring the salt to the state of simple muriate, from which a subsequent addition of muriated ammonia threw down a yellow salt.

Portions of the yellow and of the red precipitate were next slowly decomposed by heat. The metallic residue from the first dissolved totally and with remarkable facility in nitro-muriatic acid, and the solution on the addition of muriated ammonia deposited a precipitate perfectly similar to the original yellow salt. That from the last, on the other hand, required more acid, and after all there remained a portion of black powder absolutely insoluble by the acid: the solution afforded with muriated ammonia a red precipitate, the colour of which however was not so deep as that of the original precipitate. Another portion of the red precipitate was decomposed by heat; and the residue being placed within a porcelain tube, to one end of which was attached a retort with oxymuriate of potash, and to the other a balloon-receiver with water, was exposed to a strong heat, at the same time that a current of oxygen gas procured from the oxymuriate, was passed over its surface. After a time a blue sublimate passed into the receiver, and

when this ceased the platina was taken out of the tube and exposed to the action of nitro-muriatic acid. It now dissolved in the acid without leaving any black residue, and the solution was somewhat less coloured than that of the original red precipitate.

If to a solution of the metallic base of the yellow precipitate in aqua regia be added any salt of soda, the result is a soda-muriate from which sal-ammoniac precipitates a salt perfectly similar to the original yellow precipitate. But if the red triple salt be converted in like manner into a soda-muriate, and the crystals hence resulting be exposed for some time to the action of the air they will acquire a greenish hue; being then dissolved in water, and oxy-muriate of lime being dropped in, a deep-blue precipitate falls down, which being heated with borax affords a spongy metallic mass, insoluble even in aqua regia. If the solution from which the green precipitate has been separated is now treated with sal-ammoniac, a yellow precipitate is produced perfectly similar to that formed in like circumstances from pure muriate of platina. From the above and other similar results M. Descotils concludes that the red salts of platina are coloured by a distinct metal in a particular state of oxydation; that this metal, by itself insoluble in acids, considerably impairs the solubility of the platina with which it is mixed; that in different states of oxydation it presents different colours, blue, violet, and red; that this new metal is in part at least volatilizable on exposure to heat with access of oxygen, in which case it assumes the form of the blue oxide.

The most important circumstances ascertained by M. M. Vauquelin and Fourcroy,<sup>d</sup> in their examination of crude platina are the following.

Having previously separated most of the menachanite and some of the chromate of iron, by the successive digestion of the ore in nitric, muriatic, and sulphuric acids, the residue was treated by repeated portions of nitro-muriatic acid till nothing remained undissolved except a black powder amounting to about 3 per cent. of the whole. Of this black powder 33 grammes (508.2 grains) were mixed with an equal weight of potash and exposed to a strong heat; the mass was then lixiviated with water as long as any thing soluble was taken up. The portion insoluble in alkali was digested in muriatic acid, and thus by alternating the menstrua nothing at length remained undis-

solved except a few metallic grains weighing about 3 grammes. It had been observed that during each lixiviation a very pungent odour not unlike that of horse-radish was given out; in consequence of this all the alkaline solutions were mixed together and submitted to distillation with proper precautions. The fluid that came over was obtained in three separate portions, of which the first had a highly pungent odour, but the last had very little. The corks by which the bottles holding these three liquors were closed had acquired a deep blue almost black colour, and a drop of the first product having fallen on the hand of the operator communicated to it an indelible deep-brown stain. To the taste these liquors were pungent and styptic.

A few drops of tincture of galls were added to part of the distilled liquor, which immediately produced a vivid blue tinge. Into another portion was dropped some prussiate of potash, but no precipitate took place; the liquor however became red, and on the addition of a little nitric acid passed to purple. Into another portion a little muriatic acid was dropped, and a stick of zinc was put into it, the fluid first became purple, then deep blue, and at length deposited a considerable quantity of a black flocculent matter insoluble in acids. A similar change of colour was occasioned by the addition of green sulphate of iron and of sulphuretted hydrogen.

The alkaline lixivium from which the above mentioned liquor had been distilled, was next examined, and was found to contain chromic acid combined with the potash.

The muriatic solution was the next object of enquiry. For this purpose all the muriatic solutions were mixed together and evaporated to dryness, in order to separate the siliceous matter which they had taken up in considerable quantity: the residue was washed with water which took up all the metallic salts. This latter solution being filtered and moderately evaporated (by which its colour had become a deep red) was mixed with a little muriatic acid, and exposed to the action of metallic zinc. In a short time the solution became first green, then blue, and finally deposited a copious flocculent matter of a brilliant black colour. This sediment was well washed in water, and afterwards in diluted muriatic acid in order to carry away any oxide of iron that might be present; it was lastly desiccated in a moderate heat and thus acquired a considerably brilliant metallic-white colour.

<sup>d</sup> Ann. de Chim. xlix, p. 181-219. 1. p. 5.

The metal when thus purified has nearly the appearance of platina, but is brittle and may be pulverized without difficulty. When strongly heated before the blowpipe it is volatilized entirely in the form of a white vapour. The only acid that has any action on this metal is the nitro-muriatic, and even this when assisted by a boiling heat will not take up nearly  $\frac{1}{300}$  of its weight. The colour of the solution is nearly rose-red, which when almost dry changes to a very pure blue, and when perfectly desiccated returns again to its former colour.

If the metal finely pulverized be mixed with an equal weight of potash and calcined, the result is a greenish mass, which when digested in water affords a red solution, and a part not soluble in this fluid. The addition of any acid to the alkaline solution throws down the metal in the state of a flocculent red oxide. If strong muriatic acid be digested on the portion insoluble in water, it is for the most part taken up, communicating to the menstruum an intense green colour, which by dilution with water changes to blue, and by the subsequent addition of nitric acid to red. In no state does the solution afford a precipitate with prussiate of potash, provided it is entirely free from iron. Tincture of galls assisted by a little alkali changes the blue solution to a violet, and throws down a redish brown precipitate.

From these and other circumstances the authors of this enquiry draw nearly the same conclusions as Descotils does; namely that besides the known metals with which crude platina is mixed or alloyed, there is another as yet unnamed, to which the red colour of the triple salts of platina is owing, and which in all probability materially contributes to the hardness of all the specimens of this metal which have hitherto been offered to the public as pure platina.

### § 3. Physical Properties.

Dr. Wollaston in a paper recently laid by him before the Royal Society,<sup>e</sup> has pointed out a method of forming extremely thin wires of platina, which shows the remarkable ductility of this metal. He takes a globule of pure platina, hammers it into a square rod, and then draws it into a wire about  $\frac{1}{250}$  of an inch in diameter. A portion of this wire is then coated in the usual manner with silver, forming a rod about  $\frac{1}{3}$  of an inch in diameter; and this rod may again be drawn to the same degree of tenuity as the first platina wire. Hence the diameter of the platina in this compound wire is  $\frac{1}{250 \times 75} = \frac{1}{18750}$  of an inch. In order to

separate the platina from the investing silver the best way is to bend a portion of the wire into the shape of the letter U with small hooks at its upper extremities. In this form it will conveniently hang on a wire of gold or of platina with its lowest part immersed in nitrous acid, till the coating of silver is removed from that part. Platina wire of the above mentioned diameter will support about  $1\frac{1}{3}$  grain before it breaks.

### § 4. Chemical Properties.

On this head we have only to add the composition of the oxides of platina as laid down by Berzelius.<sup>f</sup> If muriate of platina is gently heated on a sand-bath till it ceases to give out oxymuriatic gas, there remains a greenish grey powder insoluble either in water or in acids. This powder is however decomposable by the fixed alkalies, which separate from it a black oxidulum that is itself soluble in an excess of alkali, forming a deep green liquor. In the oxidulum 100 parts of platina are combined with 8.28 parts of oxygen, and in the greenish-grey oxide with twice as much, or according to actual experiment, with 16.38 parts of oxygen.

It appears probable however from the insolubility of the platina, from the black deposit after the action of the alkali, and from the green colour of the alkaline solution, that the platina employed by M. Berzelius was contaminated by a mixture of iridium.

PLEONASIE, H. Ceylanite, W.

The colours of this mineral are blue and green, each so intense as to appear almost black. It occurs in rolled grains or in small crystals; which are either the regular octohedron (its primitive form) or the rhomboidal dodecahedron, perfect, or with the trihedral solid angles replaced by four facets. It rarely exhibits indications of the natural joints, the fracture being perfectly smooth and flat conchoidal, with a shining somewhat resinous lustre. It scratches quartz, but is inferior in hardness to the red spinelle. Sp. gr. 3.7.

Before the blowpipe it is infusible. The only analysis that has been made of it is by M. Collet Descotils, according to whom it is composed of

68. Alumine  
12. Magnesia  
2. Silix  
16. Oxyd of iron

98.

<sup>e</sup> Phil. Trans. 1813, p. 114.

<sup>f</sup> Ann. de Chim. lxxxiii. p. 168.

It occurs in the sand of Ceylon, and has more recently been found among the substances ejected from Vesuvius.

This substance is at present ranked by Haiiy as a variety of Spinelle, with which it agrees in its crystalline form, and differs but little in other particulars.

POTASH, *Pure, and Hydrat of.* See ALKALI FIXED.

POTASSIUM. See ALKALINE BASIS.

PRUSSIC ACIDS. PRUSSIATS.

Some additions have been made to our knowledge of this very singular class of substances, though the subject is still peculiarly difficult. What we have at present to offer relates to actual experiments and matters of fact.

*Prussiat of Potash.* The simple combinations of prussic acid with the salifiable bases were shewn by their eminent discoverer, Scheele, to be peculiarly easy of decomposition, the prussic acid being volatilized and expelled from its bases by every other acid, and even by a boiling heat when in solution. Several chemists however have attempted to prepare a simple prussiat of potash directly from the lixivium of blood, without the intervention of any salt of iron, and the following is the process of Richter.\*

Evaporate to dryness a strong solution of a pound of pure salt of tartar, or subcarbonat of potash, with 3 pounds of dried and pulverized ox-blood. When quite dry, put the whole in a covered crucible and heat it in a moderate fire till it no longer puffs up: then raise the heat to redness, and continue it till no more flame issues from the crucible. Remove the contents and lixivate them with water. This liquor is quite limpid, alkaline, and gives ammoniacal fumes. Evaporate it considerably (during which it gives out an intense bitter-almond smell, which always attends the volatilization of free prussic acid) and then add acetite of lime as long as there is any precipitate of lime produced by the excess of alkali, after which filter the liquid and boil it down till it skins over, and then set it by in a cool place. In about twelve hours many small crystals are deposited of the shape of a cube truncated horizontally, and more of the same crystals are yielded by a further concentration of the mother liquor. Collect them all, and purify them by again dissolving them in water, evaporating, and crystallizing as before, but this is attended with some waste of the prussic acid, as the same bitter-almond smell is given out, and the liquor becomes

slightly alkaline. Therefore to avoid further loss, again purify this second crop of crystals by drying them on blotting paper, washing them with some alcohol mixed with an eighth of acetic acid, and again drying them on paper.

By this process about an ounce and a half of the crystallized simple prussiat of potash is obtained. This salt has a caustic taste mixed with the same flavour of bitter almonds, and the odour of the same is perceived when the salt is dissolved in water and heated; but not when it is heated by itself. When this salt is boiled with prussian blue, a yellow solution is formed, which yields the common triple prussiat of potash and iron.

To this process of Richter the following observations are added by Bucholz.<sup>b</sup> The best proportions of the material are two parts of dried blood to one of alkali. No advantage whatever is gained by using a perfectly caustic alkali. The prussic acid is not very easily destroyed by dry heat, for much of it remains in the alkali even when it begins to fuse: but the process of evaporation should be shortened as much as possible, as the prussic acid is constantly flying off during the whole time. There is always much uncertainty in this mode of obtaining the prussic acid and a good deal of waste in every step of the operation, and even the treatment with alcohol and acetous acid, recommended at the end, does not merely saturate the excess of carbonat of potash, which is the object of this addition, but liberates much prussic acid which is thus lost.

Proust has the following observations on the simple prussiat of potash. It may be obtained either by saturating potash with the prussic acid expelled in the usual way from prussiat of mercury, or by digesting alcohol with a concentrated lixivium of potash and calcined blood prepared as above described. The alcohol gradually gains a bitter alkaline taste as it dissolves the prussiat. Generally a little hydrosulphuret of potash is contained in the lixivium, which is also dissolved by the alcohol. The prussiat of potash is then obtained in a solid state by evaporation and crystallization.

When the watery solution of this simple prussiat is boiled, it constantly parts with its acid as already mentioned, and the vapour burns when a lighted taper is brought to it. Besides which, another part of the prussic acid is decomposed in the boiling lixivium itself, producing carbonat of ammonia, which appears in a gradually encreasing quantity as the boiling is

\* An. Chem. tom. 51. p. 182.    <sup>b</sup> Ibid. page 185.    <sup>c</sup> Ibid. tom. 60.

continued. During the whole time the potash as it loses prussic acid acquires carbonic acid, so that the lixivium, which at first does not alter muriat of lime, gives an abundant precipitate of carbonat of lime after continued boiling.

All that has been observed concerning the prussic acid shews the extreme facility with which it separates from its simple union with an alkali, as Scheele has remarked.

To proceed with Proust's observations :

*Triple Prussiat of Potash and Iron, or Common Crystallized Prussiat of Potash—Prussian Blue—White Prussiat of Potash and Iron.*

The triple prussiat of potash and iron does not change on exposure to air, nor does it (like the simple prussiat) lose any acid by long boiling. It is also insoluble in alcohol. The iron which it contains is the *suboxyd*, and it is to this that it owes its property of producing Prussian blue with the *peroxyd* of iron. We are not acquainted with that prussiat of iron in a separate form which constitutes all but the alkaline portion of this triple prussiat, for though this salt is produced by Prussian blue and alkali, the Prussian blue is partly decomposed in the process, and parts with a portion of *peroxyd* of iron, which, dissolving in another portion of the alkali, forms an alkaline solution of iron at the same time.

The hydrosulphurets of potash and ammonia have no action on the triple prussiat of potash and iron, even when boiled with it.

The author gives the following improved method of producing the *White Prussiat of Iron*. Put into a phial a very dilute solution of green sulphat of iron, and keep some bits of sulphuret of iron at the bottom to preserve the low degree of oxygenation. Boil in a matrass 15 or 20 grains of crystals of triple prussiat of potash in 3 ounces of hydrosulphuretted water. When the vapour of the boiling liquid has issued for several seconds, and expelled most of the common air in the matrass, add the solution of sulphat of iron by drops, and the liquid will immediately become as white as milk, and continues so as long as the boiling is kept up. On standing a few seconds a precipitate falls to the bottom, which is the white prussiat; but then the effect of the atmosphere begins, and a blue tint forms on the surface, which gradually extends downwards through the whole mass.

*Prussian Blue.* It is an opinion, we believe, peculiar to Proust, that the prussic

acid in this compound is united not to the *peroxyd* but to the *suboxyd*, or black oxyd of iron. This substance does indeed contain a certain quantity of the peroxyd, as is proved by the conversion of the white into the blue prussiat by absorption of oxygen, but the author asserts that the same portion of suboxyd remains united to the prussic acid, as was before combined with it in the triple prussiat from which the blue prussiat is produced. Hence when Prussian blue is produced by adding the triple prussiat of potash and suboxyd of iron to any other salt of iron, it is the oxyd of the latter salt only that passes to the highest state of oxydation (if it were not so before) and the suboxyd of the triple prussiat accompanies it unchanged.

The chief reason which the author gives for this opinion of the unchangeable nature of the suboxyd whilst united with prussic acid in Prussian blue, is, that if the *peroxyd* of iron is digested with prussic acid, no combination whatever will take place, but if the *suboxyd* be used a green prussiat will be formed, which soon becomes blue by contact of the air. This last fact would indeed lead to the conclusion that the blue colour is an indication of perfect oxygenation of all the iron present, since it is produced obviously by absorption of oxygen from the air: nor is it easy to explain this experiment on Proust's hypothesis, of a mixture of suboxyd and peroxyd in Prussian blue.

It is a fact however, and was early noticed by Scheele, that the simple prussic acid, or the simple prussiat of potash, will not give any precipitate with any salts of iron, except those in which the metal is in the lowest state of oxydation; but the precipitate once being formed, a portion at least of the suboxyd passes to the state of peroxyd by absorption of oxygen, and gives the deep tint of Prussian blue.

*Prussic Gas.*<sup>d</sup> The pure gaseous prussic acid is obtained by heating in a retort triple prussiat of potash with dilute sulphuric acid. The gas may be received either in water or alcohol, or over mercury, and when either of these liquids is introduced, it will absorb the gas rapidly. The prussic gas is constantly tending to escape from the watery solution, and when the liquor is warmed so that the gas is given out rapidly, it will burn in an uniform jet of flame, when lit by a taper. The watery solution will also decompose by itself, even when kept in a closed vessel. It turns yellow in a few months and deposits a sediment of charcoal. The watery

solution of prussic gas if recent, does not trouble even the solution of green sulphat of iron, but if it has been long kept, the blue precipitate is formed, which is a triple compound of the prussic acid, of suboxyd of iron, and of the ammonia generated by the spontaneous decomposition of part of the prussic solution.

On the other hand alcohol saturated with prussic acid preserves it without change.

M. Gay Lussac has given some further particulars respecting the prussic acid, in which he shews that when free from any combination, the gas may be condensed into a peculiar liquid. Some prussic gas was prepared by decomposing prussiat of mercury with muriatic acid, and was collected over mercury. During the operation some globules of liquid came into the vessels holding the gas, and on the following day, when the temperature had fallen to 54° Fahr. the volume of prussic gas had much lessened, and more of this liquid had condensed. Another mode of preparing it was then employed: some prussiat of mercury was put in a tubulated retort, in the beak of which a bent tube was luted, the other end of which dipped into a tubulated bottle, holding a mixture of dry muriat of lime and chalk, intended to detain both the water and the muriatic acid that might come over. A tube proceeding from this bottle led to a second similar bottle containing muriat of lime, and this was joined to a ground stopper glass phial, in which it was proposed to collect the pure prussic acid. This and the two other tubulated bottles were surrounded with ice and salt. Muriatic acid was then poured into the retort, and gently heated. The prussiated mercury soon dissolved, vapours condensed in streaks on the neck of the retort, and the operation was stopped as soon as water began to be vaporized.

All the prussic acid thus obtained, usually condenses in the first bottle adhering to the muriat of lime, which last remains dry if no water has distilled over, but if any has passed, the bottle contains two unmixed liquids, of which the lower is a solution of muriat of lime in water, and the upper is the prussic acid. To rectify it, it is only necessary to remove the retort, to close the orifice where the tube from it entered the first bottle, to remove the freezing mixture from this alone, and instead, to heat it very gently not exceeding 85° or 95° Fahr. By this means the prussic acid is driven into the second bottle; and by a further rectification it may be made to pass into the third. Indeed the second bottle with muriat of lime appears superfluous, and may probably be omitted.

Prussic acid thus obtained is a limpid colourless fluid. Its taste is at the first moment cool, but soon becomes hot and acrid. Though rectified from chalk it weakly reddens litmus paper. Its density at 45° is 0.7058. It is highly volatile, and boils at 79°: at 68° it supports a column of mercury at 14.96 inches (Eng) it increases five-fold the bulk of any gas with which it is mixed. When exposed to the cold produced by a mixture of salt and snow it congeals, often into regular crystals resembling fibrous nitrated ammonia. It begins to liquify at 5°. When a drop of it is put upon paper it congeals instantly, owing to the cold produced by the evaporation of one portion reducing the temperature of the remainder.

We shall add (from Proust) a few additional observations concerning the simple prussiat of mercury. The basis of this salt is the *red oxyd* or *peroxyd* of this metal, and it differs from most of the other simple prussiats by being much more fixed, and not parting with its acid by mere solution and boiling. When prepared from prussian blue containing potash, it will carry with it part of the potash, and also some oxyd of iron. The latter may be separated by repeatedly boiling the prussiat with red oxyd of mercury, during which it deposits the red oxyd of iron which it held in solution. Prussiat of mercury readily crystallizes in tetrahedral prisms. It is totally decomposed by gradual distillation, giving a highly inflammable prussic gas mixed with oil and carbonic oxyd and acid, and about 72 per cent. of mercury. There appears to be no prussiated *suboxyd* of mercury, for when prussic acid is digested with calomel or with the nitrated suboxyd of mercury, running mercury and the common prussiat of mercury are obtained. Both the simple and the triple prussiat of potash are decomposed by red oxyd of mercury; in the latter case long boiling is required, the iron of the triple prussiat is deposited as peroxyd, and along with it some running mercury which has probably been brought to the metallic state by yielding oxygen to the iron, and the rest of the mercury unites as red oxyd to the prussic acid. Muriatic acid heated with prussiat of mercury totally decomposes it, the prussic acid is given out, and the residue is totally soluble in alcohol (which prussiat of mercury is not) and is merely corrosive sublimate.

PYCNITE. See TOPAZ.

PYROACETIC SPIRIT. See ACETIC ACID.

PYROPHYSALITE. See TOPAZ.

## S

SARCOLITE. See ANALCIME.

SCHILLERSPAR. See DIALLAGÉ.

SILEX. SILICIUM.

The existence of a pure metallic basis, of which silex is an oxyd, has been made probable by several experiments, first by the eminent discoverer of the alkaline bases, and afterwards by Berzelius and Stromeyer.

When iron is negatively electrified,<sup>a</sup> and fused by the Voltaic battery in contact with silex, the metallic globule contains a matter which affords silex during its solution. As the globule has an uniform metallic appearance, it may fairly be presumed to be an alloy of iron with some other metallic substance, which in all probability is the *basis of silex*, since silex is produced on solution of this alloy. Also when potassium is ignited in contact with silex, a compound is formed consisting of potash, in which are black particles resembling plumbago, which are supposed with probability to be the same metallic basis of silex. They are but little acted on by water, but they slowly dissolve in acids with effervescence, and when heated they burn and become converted into a white matter which is silex. This metallic basis of silex is termed *Silicium*.

Professor Berzelius has obtained this substance in combination with iron in the following way.<sup>b</sup> A mixture of 3 grammes of iron filings,  $1\frac{1}{2}$  gramme of silex, and 0.66 of a gramme of powdered charcoal were exposed for an hour to a blast furnace in a luted crucible. In the mass when cold were found small metallic reguli, which were extracted by the magnet, and cleaned on paper. Some of them were put into dilute sulphuric acid, and slowly dissolved therein when heat was applied. When all action of the acid had ceased, the forms of the globules still remained, but of various colour, and all of them when burned in open fire left a red or a white ball of silex of the same shape as the original globule. The silex amounted to about  $3\frac{1}{2}$  per cent. of the weight of the globule.

Another similar experiment was made, but with less charcoal. Equal parts of ground flint and iron filings and  $\frac{1}{5}$  of their weight of powder of charcoal were made into a paste with gum, and divided into little balls. These were packed up in powder of flints, enclosed in a luted crucible and heated as before. The globules thus obtained were less perfectly fused

than the former, but more malleable. When digested in aqua regia, the iron was dissolved with vehement action, and the acid left a white mass of silex of the form of the globules, which swelled by continued digestion with the acid, and became semi-gelatinized on evaporation. The silex in this experiment amounted to about 19 per cent. of the whole globule.

The author relates many attempts made to analyze these globules with accuracy, in order to ascertain the proportion of *Silicium* in them (supposing them to be a triple alloy of iron, silicium, and carbon) and hence, by the difference of weight between the silicium and silex, to infer the quantity of oxygen absorbed by the latter. This analysis could not be brought to a very satisfactory degree of accuracy, chiefly on account of the difficulty of finding the exact quantity of carbon, owing to a conversion of part of it into a kind of fetid oil during the action of acids, but the average results of the experiments would give the composition of silex to be about equal weights of silicium and oxygen.

A later series of interesting experiments on the same subject has been made M. Fred. Stromeyer, who has gone over the same ground as Berzelius, and with nearly similar results.<sup>c</sup> Great care was taken to select very pure iron, silex, and charcoal, the latter was pure lamp-black, to avoid the small proportion of potash which all wood charcoal gives when burnt. The whole was made into a paste with linseed oil, and heated most intensely for an hour in a luted hessian crucible. As to the respective proportions of these three ingredients, the author found from many trials most uniform success from 5 parts of silex, 7 of iron, and from 0.25 to 0.8 of lamp-black. With from 0.25 to 0.5 of the lamp-black the alloy remained more or less ductile, but where it exceeded 0.5 it was brittle. Much difference however was found between the globules of alloy resulting from the very same operation, in their size, colour, lustre, ductility, and also in their composition, so that the effect of the fusion is very unequal in the different parts of the same crucible.

The specific gravity of these globules of alloy varied from 6.77 to 7.32, and was always much inferior to that of the iron used, which was 7.828. The author describes several varieties in the texture and other sensible properties of

<sup>a</sup> Davy's Elements.

<sup>b</sup> Phil. Mag. No. 173. From the original Swedish.

<sup>c</sup> Ann. Chim. tom. 81. From the Gottingen Transact.

these globules. One of these bears a very strong resemblance to common steel, and like steel it becomes hardened by being quenched in water when red-hot, and it also assumes the usual shades of colour on being heated to different degrees. All the varieties of this alloy are harder than forged iron, and take a very high polish, and also are perfectly magnetic.

M. Stromeyer gives the particulars of the analysis of every variety of these globules of alloy, which is rendered difficult for the reason already mentioned, namely the uncertainty in estimating accurately the carbon. Nevertheless he finds full reason to infer the probability of the existence of *Silicium* for the following reasons, viz.

That the iron and silix extracted from the alloy (estimating the iron in the reguline state) when taken together very sensibly exceed the weight of the alloy examined, even making no allowance for the carbon: that the alloy gives a much greater quantity of hydrogen with muriatic acid than the iron alone which it contains would give: that there is no known mechanical or chemical combination of a metal with an earth, which requires the successive operation of the most powerful reagents to decompose as this alloy does; and that the iron retains its malleability in this alloy, this property being apparently only affected by the proportion of charcoal present. For all these reasons therefore it appears hardly to be doubted that it is the metallic basis of silix, and not the earth itself which enters into this triple alloy.

The general mean results of these experiments give the composition of silix to be 46 per cent. of silicium, and 54. of oxygen.

In the different varieties of the above-mentioned alloy, the component parts of the most brittle, which is termed the *lamello-granulated silicio-carburetted iron*, are 85.352 of iron, 9.268 of silicium, and 5.38 of carbon: and the most ductile contains 96.178 of iron, 2.212 of silicium, and 1.61 of carbon: the silicium therefore varies from about 2.2 to 9.2 per cent. The alloy is sub-ductile when the silicium does not exceed 3 per cent.

#### SILVER.

For some further observations on the composition of the oxyd and muriat of silver, see the article *Affinity* in this appendix.

SODA, pure, and hydrat of. See ALKALI FIXED.

#### SODALITE.\*

This mineral occurs massive and crystallized

in rhomboidal dodecahedrons. Its colour is bluish green. It exhibits joints in at least two directions. Its longitudinal fracture is foliated with a shining resinous lustre; its cross fracture is conchoidal with a vitreous lustre. It is translucent, yields with difficulty to the knife. Sp. gr. about 2.37. When heated to redness it acquires a dark grey colour; it is not fusible *per se* before the blowpipe.

It has been analyzed by Dr. Thomson and M. Ekeberg, with the following results.

T.	—	E.	
38.52	—	36.	Silix
27.48	—	52.	Alumine
23.5	—	25.	Soda
3.	—	6.75	Muriatic acid
1.	—	0.25	Oxyd of iron
2.70	—	—	Lime
2.1	—	—	Volatile matter
—	—	—	—
98.3	—	100.0	
1.7	Loss	—	

It occurs in Greenland associated with sah-lite, augite, hornblende, and garnet.

SODIUM. See ALKALINE BASIS.

SPINELLE *Zinciferous*. See AUTOMALITE.

#### SPINELLANE.

This mineral occurs in minute rhomboidal crystals of a blackish-brown colour. It scratches glass, and when exposed to the blowpipe becomes first white and then fuses without difficulty into a white very frothy enamel. It has been found by M. Nose on the border of the lake of Laach, in a rock composed of grains and small crystals of glassy felspar, of quartz, hornblende, black mica, and magnetic iron ore.

#### STILBITE.

It occurs crystallized or fasciculated. Its form is a four or six-sided prism, truncated, or with pyramidal terminations, the faces of which are unequally inclined with regard to each other. It is transparent, translucent, and sometimes almost opaque. Its colour is white, grey, or brown, with a pearly lustre. It exhibits natural joints only in one direction: its cross fracture is uneven, glimmering. It scratches calcareous spar, but is softer than glass. Sp. gr. 2.5.

It is not electric by heat; by digestion in cold nitric acid it swells, but does not gelatinize. On exposure to the blowpipe it first exfoliates, and then melts with ebullition and phosphorescence into a white enamel.

\* Thomson in Phil. Journ. xxix. p. 288.



According to an analysis of this mineral by Vauquelin, it is composed of

52.	Silex
17.5	Alumine
9.	Lime
18.5	Water
<hr/>	
97.0	
3.0	Loss

It occurs sometimes in mineral veins, but generally filling cavities in amygdaloid.

STONE METEORIC. See AEROLITE.

SUGAR.

A singular mode of converting starch and other insipid vegetable matter into a highly saccharine matter has been discovered by M. Kirchoff of St. Petersburg, and amply confirmed by subsequent trials.

It consists simply in boiling a solution of the starch for many hours with a small quantity of sulphuric acid, during which the mixture will gradually acquire a sweetish taste, and this saccharine quality encreases to a certain point, after which the acid (which does not appear to be decomposed in the process) must be saturated with lime, and separated in the form of sulphat of lime, and the remaining liquid which is then a rich syrupy mass, may either be evaporated to dryness, or (by way of experiment) may be mixed with yeast and fermented, and will then yield a considerable quantity of ardent spirit by distillation. It does not appear however that a very pure crystallized sugar has ever been obtained in this way, though the saccharine mass has both the taste and the most important chemical properties of sugar.

M. Kirchoff's original experiment is the following.<sup>a</sup> Take 100 lbs. of starch, 400 lbs. of water, 1 lb. of sulphuric acid, and some powdered charcoal and chalk. Mix the acid with half the water, bring it to boil in a well tinned copper; rub the starch with the rest of the water, pass it through a sieve, and add it by six ounces at a time to the boiling acid and water. Then continue the boiling for 36 hours, adding fresh water to supply the waste by boiling. Afterwards add a little charcoal powder and chalk sufficient to saturate the acid, and pass through a linen cloth the liquid which is now clear and sweet. Evaporate it by a gentle heat to the consistence of syrup, and set it by, that the sulphat of lime may crystallize. Remove this, strain the liquid part and again set it by, when the rough sugar will separate in about three days. This may be pressed with ease

from the adhering syrup, and by being again dissolved and crystallized, will become much purer.

If a greater quantity of sulphuric acid is employed, the boiling must be continued longer.

Not only the sulphuric, but the muriatic and some of the other acids will thus convert starch into sugar, but the sulphuric is by much the most convenient, as when it has performed its office, it may be removed with great ease by means of lime.

M. Kirchoff's experiment has been repeated much at large by M. Vogel.<sup>b</sup> Some starch was first washed with cold water merely to purify it; then 2000. parts of it rubbed with 8000 parts of water acidulated with 40. parts of sulphuric acid, were boiled for 36 hours in a silver vessel (which is much better than one of copper or tin) with stirring, at first constant, afterwards only occasionally. The process was conducted as above described, and a quantity of rich syrup about equal to the starch employed was obtained. M. Vogel also got an equal quantity from twice the proportion of acid, and only eight hours boiling. This syrup boiled down slowly in tin moulds gave a solid transparent elastic mass, which attracted moisture from the air. A portion of it mixed with yeast and fermented, yielded alcohol by distillation.

A similar saccharine gummy mass was obtained from potatoe starch. This was further analyzed by boiling alcohol, which left undissolved about a fifth of the whole in the form of a viscous matter much resembling gum arabic when dry, but differing from it in not forming the mucous acid when treated with the nitric.

M. Vogel then tried the effect of a similar boiling with sulphuric acid upon sugar of milk, which though saccharine to the taste is not capable of the vinous fermentation: 100 parts of sugar of milk, 2 parts of strong sulphuric acid, and 400 parts of water were boiled together only for three hours, and the excess of acid neutralized by chalk. On evaporating the clear syrup it concreted in a few days into a rich saccharine mass, which *now* would ferment on adding yeast, and yielded alcohol by distillation.

Muriatic acid was found to have the same effect as the sulphuric upon sugar of milk, but not the nitric or acetic acids.

We shall relate another experiment on the same subject, performed by Dr. Tuthill, as it appears to have been made with great attention.<sup>c</sup> One pound and a half of potatoe starch, six pints of distilled water, and a quarter of an ounce, by weight, of sulphuric acid were boiled

<sup>a</sup> Journ. de Physique for March 1812, or Retrospect, No. 33.

<sup>b</sup> Ann. Chim. tom. 82.

<sup>c</sup> Phil. Journ. vol. 33.

together in an earthen vessel for thirty-four hours without intermission, the waste by evaporation being supplied by fresh water, and frequent stirring being used to prevent the material from burning. The liquid had become sensibly sweet to the taste at the end of twenty four hours, and this sweetness increased as long as the boiling was continued. At the end of this time, half an ounce of finely powdered charcoal was added, and the boiling continued two hours longer. The acid was then saturated by lime, the boiling continued half an hour longer, the liquid strained through cloth, and the residue rinsed in warm water. This latter, when dry, weighed  $\frac{7}{8}$  of an ounce, and consisted chiefly of charcoal and sulphat of lime. The filtered liquid was then evaporated in a water-bath to the consistence of syrup, and set aside. In eight days it had concreted to a crystalline mass, tasting like a mixture of brown sugar and treacle. One pound of this sugary matter was then dissolved in four pounds of water, a quarter of an ounce of yeast was added, the mixture was fermented, distilled and rectified, and gave a weak ardent spirit, which from Blagden's tables was found to contain 14 drams by measure of proof spirit. The whole amount of the saccharine matter was  $1\frac{1}{4}$  lb., the produce of  $1\frac{1}{2}$  lb. of starch from  $8\frac{1}{4}$  lbs. of potatoes.

Such are the facts of this singular process. The explanation of it is very obscure. It might at first be supposed that the sulphuric acid was decomposed by the vegetable matter, but from the experiments both of Vogel and Bouillon La Grange,<sup>d</sup> it appears that this is not the case. Not only is no sulphureous acid generated, but no sign of acidity whatever is given by the liquid condensed from the vapour of these materials when boiling, (which is mere water) and besides it appears that the acid remaining in the syrup after the long boiling, will saturate as much of any base as it would have done before mixture with the starch.

Some chemists have suggested that the mere effect of heat on the starch might convert it into sugar independently of the acid, but on trial, by boiling starch and water together for four successive days a liquid mass was obtained, not in the smallest degree saccharine, but only a bitter mucilage.

La Grange made the experiment of boiling 100 grammes of sugar of milk, 4 grammes of sulphuric acid, and 400 grammes of water, in a retort, and collecting all the products. No gas whatever was given out but the air of the vessel. A given quantity of potash was then added to

saturate the acid, and the whole was evaporated to dryness. It was then weighed, and amounted only to 98 grammes. This experiment was repeated several times with a very close resemblance in the results, the loss of weight being at times a little more or less, but always much more than the water originally added, and that which might exist in the sulphuric acid.

The inference which the author makes is, that as no gaseous product was given out, and as no liquid but water distilled over, this loss of weight can only be accounted for from the production of a quantity of water from the sugar of milk employed. A similar result took place with starch. Hence it would appear not improbable that when starch, sugar of milk, &c. lose a certain quantity of hydrogen and oxygen (in the same proportions in which these constitute water) they approach to the nature of sugar. Some light may be thrown upon this subject by the *Analysis of Vegetable Matter* (given in this appendix) conducted by Gay Lussac and Thenard, by which these eminent chemists appear to have proved that all these vegetable matters, namely starch, sugar of milk, mucilage, &c. consist merely of carbon and water, or its two materials in their proper proportions, and hence the sole abstraction or addition of water assisted by some powerful chemical reagent, may convert one into the other.

SULPHUR, ALCOHOL OF. LIQUID CARBURETTED SULPHUR.

In 1796, M. Lampadius distilling martial pyrites with charcoal, obtained a very singular liquor, to which he gave the name of *Alcohol of Sulphur*, and considered it as a compound of sulphur and hydrogen.

Messrs. Clement and Desormes, some years after, obtained the same liquid by passing the vapour of sulphur over well dried charcoal ignited in a porcelain tube, and from the result of many experiments, they considered this fluid as a compound of two thirds sulphur, and one third charcoal, whence they termed it *Carburetted Sulphur*, and denied the existence of hydrogen as a constituent part.

Afterwards M. Amedée Berthollet, in a very elaborate and skilful series of experiments on this fluid, was led to conclude that it contained no charcoal whatever, but was produced by the union of sulphur and hydrogen in variable proportions.

Some experiments made by M. Vauquelin on the same substance have led this eminent chemist to a similar conclusion with that of Messrs. Clement and Desormes. Lastly, M. Cluzel in

<sup>d</sup>. Ann. Chim. tom. 82.

a very elaborate memoir, read at the Institute in December 1811, has considered this liquor as a quadruple compound of charcoal, hydrogen, azote, and about half its weight of the *Radical of Sulphur*, considering sulphur itself as a protoxyd of this unknown radical.

We shall give a short account of the experimental part only of these different enquiries.

The different processes for obtaining the alcohol of sulphur are the following.

Lampadius procured it accidentally by distilling together pyritous peat, and pyrites with charcoal.

Clement and Desormes give the following process.<sup>a</sup>

This substance is obtained by passing sulphur through a porcelain tube heated to redness, which is filled with charcoal, partly in powder, and partly in lumps, and previously heated. The charcoal should be heaped pretty close.

The apparatus used, was the porcelain tube holding the charcoal and placed a little slanting across the furnace. To the upper end of the porcelain tube, a long and wide glass tube is cemented, holding a series of small cylinders of sulphur, which can be successively pushed forwards into the other tube by an iron pin which passes through the cork that shuts the upper end of the glass tube. To the lower end of the porcelain tube is fitted a glass adopter terminated by a bent tube, dipping in a tubulated bottle of water, which also communicates with the pneumatic trough.

The charcoal should be first strongly ignited till all the gas which it spontaneously yields is given off, then the bits of sulphur should be gradually pushed down, and by their action upon the heated charcoal, a yellowish oily limpid fluid condenses in the adopter. As the process continues, and the adopter becomes heated, the fluid is partly volatilized, but is again caught in the further bottle at the bottom of the water, where it collects in globules. Some care is required not to push on the sulphur too hastily, otherwise much of it passes through unchanged, and is apt to block up, and sometimes to break the tube of the glass adopter. No gas whatever escapes whilst the alcohol of sulphur is forming, except the expanded air of the apparatus. The alcohol of sulphur may be obtained, though with difficulty, by heating together charcoal and sulphuret of antimony.

The directions given by Vauquelin<sup>b</sup> for the preparation of the liquid, differ but little from the former. The bottle that receives the fluid

should be connected with another bottle, and surrounded with snow or bits of ice to keep the water quite cool, as the alcohol of sulphur is very volatile. It is of use also to cut a notch at the bottom of the tube that dips in the water of the first bottle, to serve as a tube of safety to prevent the hot porcelain tube from cracking by any regurgitation of water into it. By using two bottles, and keeping the furthest at a freezing temperature, all the alcohol of sulphur is condensed. In the operation the porcelain tube should be kept white hot, and the sulphur added very gradually. If too much of it passes at once, a portion of it unites with the condensed alcohol of sulphur, giving it more colour and density, and rendering it partially concretescible when it touches the water. As soon as the sulphur begins to act on the charcoal, a large quantity of sulphuretted hydrogen is disengaged, but this ceases almost entirely as soon as the alcohol of sulphur condenses.

M. Amedeé Berthollet<sup>c</sup> prepares the alcohol of sulphur nearly in the same way as that last mentioned. The tube in which the mixture is made is of glass, and about 40 inches long; it is laid a little inclined across a furnace, the lower end projecting from the sides of the furnace only about 4 inches, and the upper end about 20 inches. The part inclosed within the furnace is covered with a very refractory fire-lute. The upper end is filled with flowers of sulphur, and then sealed hermetically. The middle is filled with charcoal; and the lower end is cemented to an adopter fitting into a small tubulated receiver, which communicates by a tube with a double tubulated bottle half filled with water, one tube of which conveys the gas after passing through the water of the bottle into the pneumatic trough. The charcoal in the tube is then intensely heated, after which the sulphur is melted gradually so as to flow down into the charcoal.

As soon as the sulphur and charcoal are in contact with each other, a copious disengagement of gas takes place, and at the same time the adopter becomes filled with white vapours, which condense into the yellowish limpid liquid, which is the alcohol of sulphur. When the object of the experiment is only to form this alcohol, the charcoal should be kept only at a cherry-red, and the influx of sulphur should be very slow. The production of the alcohol of sulphur ceases spontaneously after a time, unless the heat is raised very intensely, when the flow of the liquid is renewed.

<sup>a</sup> Ann. Chim. tom. 42. p. 136.

<sup>b</sup> Ann. Chim. tom. 61. p. 145.

<sup>c</sup> Mem. d'Arcueil, tom. 1.

The charcoal should have been previously heated red-hot in a crucible for half an hour, to expell all the gasses which it usually gives out on the first impression of the fire.

M. Cluzel<sup>d</sup> in his very elaborate memoir on this substance, finds that it may be easily prepared by mixing pyrites pulverized and heated to expell all the moisture, with twice its weight of charcoal, previously calcined by itself in a close vessel for a considerable time, putting the mixture in an earthen retort, and heating it very intensely, and receiving the product in water cooled by ice externally.

The physical and chemical properties of the alcohol of sulphur are the following. It is a limpid fluid either colourless or with a slight tinge of green or yellow, which may be entirely removed by redistillation: its specific gravity is 13. water being 10. Its smell is very strong, fetid, sulphureous, and pungent; its taste is very sharp and cool. When exposed to the air it evaporates full as soon as rectified ether, and produces a more intense cold. It kindles readily when brought near any burning body, and gives a large white flame yellowish at last, and spreads a suffocating smell of sulphureous acid, and its vapour during combustion deposits on the adjacent bodies a yellow substance exactly resembling sulphur. It leaves a black residue, combustible and resembling charcoal.

The water in which the alcohol is condensed during its preparation, seems to hold a very small portion of it in solution sufficient to retain the peculiar smell, and the property of precipitating several metallic solutions; those of lead giving an orange yellow precipitate, those of corrosive sublimate, a white, and those of tin, brick red: it does not redden litmus. Ammonia dissolves it with some ease and becomes of a yellow colour, which it gives to all metallic precipitates made with this alkali thus altered. If some of the alcohol of sulphur is put in a vessel of water and the vessel is put in an air pump, when part of the atmospherical pressure is removed, the alcohol assumes the form of gas which rises through the body of the water in large bubbles, and if the pressure is restored they immediately condense again on the water, and fall to the bottom unmixed with it.

If a little alcohol of sulphur is passed up a barometer that stands at 30 inches the mercury immediately falls to 19.6 inches, at 55°. therm. so that this fluid could not exist in any but a

gaseous state at a pressure of no more than about 10.4 inches.

Alcohol of sulphur is not altered by passing through a red-hot tube, but its heated vapour burns with ease in common air when kindled. On the other hand oxygen holding the vapour of this fluid in solution, detonates with extreme violence.

Nitrous gas impregnated with the vapour of this fluid burns with uncommon splendour equal to zinc. Alcohol of sulphur will dissolve a little more sulphur without much apparent change, except in colour, which is rendered yellower.

When alcohol of sulphur is heated with a solution of fixed alkali confined in a strong vessel to prevent the escape of the alcohol, it entirely dissolves in the alkali, except a little charcoal, and a deep amber coloured liquid results, which gradually becomes a solution of sulphuretted hydrogen.

The nitric, muriatic, and sulphuric acids have no action on it in the cold. When heated, nitric acid partly decomposes it. Sulphureous acid gas and alcohol of sulphur heated together, only produce a mixed gas. Oxymuriatic acid slowly decomposes alcohol of sulphur. It dissolves easily in warm olive oil, some charcoal is deposited, and the mixture crystallizes speedily and regularly. Alcohol added to alcohol of sulphur immediately resolves it into two portions, one of which is a perfect solution and is precipitable by water. Ether also causes one portion to crystallize immediately and dissolves the rest.

Much difference of opinion exists on the composition of alcohol of sulphur. Messrs. Clement and Desormes consider it as a simple combination of sulphur and charcoal, and as they find no sulphuretted hydrogen, they consider it as a proof of the absence of hydrogen altogether. The absence of sulphuretted hydrogen they consider as proved by the total condensation of the alcohol of sulphur, when after having been vaporized through water by abstracting three fourths of the pressure of the air, this pressure is again restored. Sulphuretted hydrogen under similar circumstances would be dissolved in the water through which it is vaporized, and water thus saturated would give up very little of the gas under such a diminished pressure.

Another proof of the absence of sulphuretted hydrogen is this: if a little of the alcohol of

<sup>d</sup> An. Chim. tom. 83 and 84.

sulphur is put into a vessel containing a solution of acetated lead and part of the atmospherical pressure is removed, the alcohol of sulphur is vaporized through this solution without blackening it. If the alcohol is long shaken with the solution it finally becomes brown but not black.

M. A. Berthollet on the other hand considers this singular substance as a compound of hydrogen and sulphur only. He observes that no residue is left on burning it in the open air, but if the combustion is stopped, no other solid appears than pure sulphur. He considers the existence of hydrogen in this liquid as sufficiently proved, by the water through which it is vaporized acquiring all the properties of sulphuretted hydrogen. He is unable to detect any charcoal in the residue that is left after the spontaneous evaporation of all the volatile part of this liquid, but asserts that it is mere sulphur which may be totally sublimed. He observes that this substance when gassified and mixed with oxygen gas, detonates most violently so as to break very thick glass vessels; but by employing a very small quantity and detonating over lime-water, no precipitate is produced. Further, if some of the liquid is digested with oxymuriatic acid, the latter loses its smell; and if fresh quantities of the acid are successively added, a solid residue is finally left, which has the colour and consistence of sulphur, but in which no charcoal can be discovered. Neither is any charcoal removed by the oxymuriatic acid, for no carbonic acid is generated by its action.

He likewise observes that a solution of potash shaken with a little of the alcohol of sulphur finally becomes a hydro-sulphuret of potash, with an excess of sulphur, but no charcoal nor carbonic acid appears. When alcohol of sulphur is distilled with water at a heat of 86° to 96° Fahr. and in an apparatus quite free from air, the first product is a gas exactly similar to that produced by the spontaneous evaporation of the liquid, which has the smell of sulphuretted hydrogen, burns blue in the air, detonates strongly with oxygen, is speedily absorbed by water, rendering it milky by the deposition of sulphur, and produces a solution resembling entirely that of sulphuretted hydrogen. After this gas has passed away a transparent colourless fluid comes over, which swims in drops on the surface of the water. If the heat is raised to 112° and kept up for some time, all that remains of the alcohol of sulphur is a mass

that crystallizes on cooling, and may finally be sublimed like sulphur.

Several apparent varieties of the alcohol of sulphur are found according to the rapidity with which the sulphur is sent through the hot charcoal; all these the author considers as different combinations of sulphur and hydrogen in various proportions.

Besides the gas and the liquid alcohol of sulphur obtained in the process of subliming sulphur through hot charcoal, a good deal of the sulphur frequently passes through, and congeals on cooling. This sulphur M. A. Berthollet observes differs from common sulphur which has been merely melted, being lamellar, light, puffy, of a golden yellow, and when again fused giving out sulphuretted hydrogen gas, and containing no charcoal. This therefore he considers as a *Solid Hydroguretted Sulphur*. In this respect it resembles the precipitated sulphur produced by the action of an acid on a solution of an alkaline sulphuret.

The source of the hydrogen in the formation of this liquid the author attributes to the *Charcoal*, which though previously heated *per se* most intensely, is still able to furnish hydrogen to the sulphur sublimed through it. The charcoal also retains a portion of the sulphur after the operation; so that the author's opinion is that charcoal consists of pure carbon and hydrogen; and the sulphur coming in contact with it at a high temperature decomposes it, the greater part of the sulphur carrying off the hydrogen and condensing into the alcohol of sulphur, the sulphuretted hydrogen, and the solid hydroguretted sulphur that are produced; and a small portion of the sulphur remaining combined with the charcoal. The author also admits in order to account for the evident erosion of the charcoal, that the gas obtained from the solid product of the distillation, contains a portion of charcoal which is made manifest by combustion.

A very elaborate analysis of this singular liquid is given by M. Cluzel,\* some of the particulars of which we shall relate. The mode of preparing it has been already mentioned. The liquors obtained by several successive operations were all united and rectified by a second distillation, which appears to make some slight alteration in some of its properties. This rectified alcohol of sulphur is totally and largely soluble in common alcohol; and the solution when dropped into water, at first renders it milky, but a large excess of water redissolves

\* An. Chim. tom. 83 & 84.

the precipitated portion, in which respect it resembles a solution of essential oil in alcohol; and which also proves that the precipitate which renders the water milky is not sulphur.

M. Cluzel employed the same method for the analysis of this liquid which was originally used by Dr. Priestley for the analysis of spirit of wine, namely, by passing it in vapour over heated copper. Copper wire was introduced into a glass tube, with a small retort containing the alcohol of sulphur at one end, and an adopter and tabulated matrass at the other. The liquid was gradually vaporized over the heated copper. No gas was produced, and only a portion of the liquid was decomposed, the remainder condensing on the other extremity of the apparatus, but somewhat altered in appearance, being of a rose-colour, very acrid and volatile. The copper when withdrawn was become brittle and covered with a black matter resembling charcoal. By further analysis it was found to be a sulphuret of copper mixed with charcoal. The copper increased from  $\frac{1}{6}$  to  $\frac{1}{5}$  in weight in the different experiments, and the copper, sulphur, charcoal, and undecomposed liquid together made up the sum of the weights of the alcohol of sulphur and copper employed, within about  $\frac{1}{5}$ th. of the whole.

The author substituted iron for copper with the hope of decomposing the whole of the alcohol of sulphur, but without success, a considerable portion of the liquid being condensed on the other side of the apparatus into the rose-coloured fluid already mentioned. He then endeavoured to analyze the liquid by combustion with oxygen gas in Volta's eudiometer, which would furnish sulphuric or sulphureous acid, carbonic acid, and water, in case the liquid was a hydro-carburetted sulphur.

M. Cluzel gives a new and very useful method of separating dry sulphureous and carbonic acid gasses; it is simply by the addition of a few bits of borax, which in less than an hour totally absorbs the sulphureous acid gas and leaves the carbonic acid untouched. The gassified alcohol of sulphur was then detonated with oxygen, and the results were sulphureous acid, carbonic acid, and a little water. We shall not follow the very complicated calculations required to deduce just inferences from this experiment, which was several times and very carefully repeated. But the author deduces from these the singular result, that the charcoal and sulphur if estimated from the

allowed proportions in the carbonic acid, and sulphureous acid produced, would when added to the hydrogen of the water sensibly exceed the weight of the alcohol of sulphur employed. Hence he is led to infer that either sulphur or charcoal or perhaps both, in the state in which we know them, must be compound bodies, probably oxyds, and that they exist in their simple state in the alcohol of sulphur here examined. Besides radical sulphur, radical carbon and hydrogen, M. Cluzel finds a small quantity of azote in this liquid; and he also finds some difference in the relative proportions of these substances in the alcohol of sulphur, and the rose-coloured liquid above mentioned.

Experiments on the analysis of this singular liquid by means of copper, have been made by M. Vauquelin,<sup>f</sup> in illustration of those of M. Cluzel.

On 55 grammes of copper made red hot in a porcelain tube, were passed 23.135 gr. of the alcohol of sulphur reduced to vapour: 4.5 gr. of the liquid escaped decomposition, and was condensed in a bottle surrounded with ice; and about half a litre of gas was disengaged, which was only the air of the apparatus saturated with the gassified liquid, as it burned with a blue flame, and the residue of the combustion precipitated lime-water in flocculi, had the odour of sulphureous acid, but did not blacken acetite of lead, and therefore contained no sulphuretted hydrogen. After the experiment the copper was found entirely sulphuretted, and of a brilliant black colour, but quite homogeneous. Its weight was 72 gr. and therefore the copper had increased 17 gr. in weight, which added to the 4.5 gr. of undecomposed liquid, leaves 1.6 gr. for the quantity of the liquid wafted away in gas in the air of the apparatus. The 4.5 of undecomposed liquid was then passed over 20 gr. of fresh copper, and this time no gas whatever was produced, so that the whole 4.5 remained in union with the copper. Hence it is inferred that if the copper is in sufficient quantity and the liquid be slowly vaporized through it, the whole would remain in union with the copper: and therefore an analysis of the black sulphuret remaining after the operation is sufficient to discover all the contents of the decomposed alcohol of sulphur. 10. grammes of the black sulphuret of copper were heated with nitric acid, which separated the metal, leaving 1.31 of a light black substance. The latter was then sublimed in a vessel filled with carbonic acid to

<sup>f</sup> An. Chim. 83. tom. p. 268.

prevent combustion, and yielded flowers of sulphur, leaving behind  $\frac{34}{100}$  of a black substance, which burnt like charcoal without any sulphureous smell, and left only a minute residue of copper.

The nitrous gas arising from the decomposition of the black sulphuret by the nitric acid, was found to contain no carbonic acid, as it did not render barytic water turbid. The sulphur sublimed from the black mass was collected, and that converted into sulphuric acid during the nitrous solution, was estimated by means of a barytic solution, and the quantity of sulphur thus obtained (allowing 41 per cent. of sulphur in sulphuric acid, and  $\frac{34}{100}$  per cent. of acid in sulphat of barytes) together with that of the charcoal actually procured, was almost exactly equal to the increase of weight acquired by the copper in the first experiment. This slight difference of weight is so small as to be easily accounted for by the necessary loss in these operations, so that M. Vauquelin considers the alcohol of sulphur as containing no hydrogen, but as consisting merely of about 14 or 15 of charcoal, and 85 to 86 of sulphur.

The rose-coloured liquid obtained by M. Cluzel gave results almost exactly the same.

Therefore if this analysis be correct, it appears that this substance is accurately termed *Liquid Carburetted Sulphur*, that it contains probably no hydrogen, and no azote, but consists of six parts by weight of sulphur to one of charcoal.

A very valuable series of experiments on this singular liquid, the result of the united labours of Professor Berzelius and Dr. Marcet, together with experiments on the production of cold by its evaporation, by Dr. Marcet, have lately been published, from which we shall extract the following particulars, omitting chiefly those circumstances in which the observations of these eminent chemists confirm those of their predecessors in this enquiry.<sup>a</sup>

This liquid was prepared by slowly volatilizing sulphur through red hot charcoal in a porcelain tube, and condensing the product in water. The fluid thus procured is at first of a pale yellow colour, and must be rectified by a second distillation.

Dr. Marcet advises the employment of a large earthen tube about one inch and a half in diameter, instead of the small porcelain tubes commonly employed. The process is always tedious, but with the large tube about half a pint of the

liquor may be procured in the course of a day. The same tube can hardly ever be used twice. Fresh sulphur may be successively introduced whilst the distillation is going on, and without renewing the charcoal, as the occasional admission of air does not materially affect the process.

To rectify the liquid it must be distilled in a heat not exceeding 100° or 110°, and to prevent any moisture from rising, some muriat of lime may also be put into the retort. The liquid must be condensed in a receiver cooled with ice. Some sulphur remains in the retort. The specific gravity of the rectified liquid is 1.272; its expansive force at 30 in. bar. and 53.5° therm. is equal to the pressure of 7.36 inches of mercury, so that air to which it is admitted will dilate about one fourth of its volume. It boils briskly at 105° to 110°. It does not congeal at 60° below 0. It burns with a bluish flame, but without the deposition of any moisture.

The volatility of this liquid is very remarkable, being superior to that of ether; and hence it produces a greater degree of cold by evaporation than any other known fluid, as will be soon noticed.

This carburetted sulphur readily dissolves in alcohol and ether, and if it contain sulphur in solution, the latter is rapidly separated in spicular crystals. It readily mixes with and dissolves all oils and camphor. Neither mercury nor silver nor lead are at all altered by this liquid, provided it has been carefully rectified, to exclude the sulphur which it holds merely in solution when first prepared. The alkalies dissolve this liquid slowly, but totally.

The first set of experiments on the composition of this carburetted sulphur here described, have for their object to determine whether it contains any hydrogen. Some of the liquid was suffered to evaporate in oxygen gas of known purity, and previously dried by muriat of lime. This vapour-holding oxygen was exploded by the electric spark which acted vividly, and  $\frac{1}{5}$  to  $\frac{1}{6}$  of its volume disappeared, at the same time that traces of a condensed fluid appeared in the vessel, which soon produced as many white specks of sulphat of mercury. This experiment not being decisive, another mode was tried. Some dried oxymuriatic gas was passed through some of this liquid, and afterwards through water. The liquid absorbed the gas readily and abundantly, and acquired an orange hue, and a very peculiar smell. The water in which most of the liquid was condensed, contained a little muriatic and a vestige of sulphuric-

<sup>a</sup> Phil. Trans. for 1813.

acid. But the greater part of the liquid remained unchanged after the absorption of the oxygen. In some days however it gradually acquired the smell of muriated sulphur.

Some of the liquid was passed in vapour through fused muriat of silver at a low red heat, but no change whatever appeared to take place in either substance. Hence they infer that the liquid contained no hydrogen, since if it had, the muriat of silver would have been decomposed, the hydrogen would have formed water with the oxygen of the muriat, and this would have united with a portion of the muriatic acid, and expelled it in the form of muriatic acid gas, with production of sulphuret of silver.

Various metallic oxyds, such as red oxyd of iron, oxyd of manganese, and oxyd of tin were ignited, and caused to receive in that state the vapour of the liquid, which was thus entirely decomposed, the metallic oxyds being converted to sulphurets, and the gasses acquiring a strong smell of sulphureous acid, but in none of these cases was any water produced.

From all these experiments, these chemists conclude that the carburetted sulphur contains no hydrogen.

The presence of carbon was the next point to be ascertained. For this purpose the gaseous residue of the combustion of the vapour of the liquid with oxygen gas was put in contact with water, and most of it absorbed, giving the water the taste and smell of sulphureous acid. Lime water absorbed part of the remainder, producing carbonate of lime; and the unabsorbed portion was detonated with fresh oxygen, and then produced a second precipitate with lime-water. This latter portion therefore was a gas that wanted more oxygen to become carbonic acid, or *Carbonic Oxyd*, and the two other portions were carbonic acid and sulphureous acid gas.

In attempting to fix the proportions of sulphur and carbon in this singular liquid, very considerable difficulties occurred, owing to its extreme volatility, and the imperfect action which the common modes of decomposition appeared to produce.

The method that succeeded the best was the following. A coated glass tube was laid in a sloping direction through a small furnace; to the upper end of the tube a small glass capsule containing some of the liquid was hermetically sealed; and to the lower, was fixed another small glass tube expanded in the middle and bent at the further end to convey any gas to the mercurial trough. The larger tube, which was laid across the furnace, was filled with red oxyd

of iron coarsely pulverized, and the bulbous expansion of the lower tube was kept surrounded with ice and salt. The larger tube being made red-hot, and the upper capsule containing a weighed quantity of the liquid carburetted sulphur, the latter was heated very gently by a lamp placed near (but not beneath) it, and its vapour was made to pass slowly through the red-hot oxyd of iron. The process was so gradual, that it required six hours and a half to volatilize and decompose about 15 grains of the oil. Some previous trials had failed from hastening the process.

In this way the decomposition was so perfect that not a particle of the liquid sulphuret was condensed at the lower end of the apparatus, but the oxyd of iron (weighing ten times the liquid used) was partly converted to sulphuret of iron, having a yellow colour and a brilliant metallic lustre. This sulphuret was dissolved (and we presume totally oxygenated) by nitromuriatic acid, the oxyd of iron separated by ammonia, and the sulphuric acid generated from the sulphur was combined with barytes by adding muriatic acid and muriat of barytes, and the sulphat of barytes washed, ignited and weighed. The mixed gas produced in the process was exposed for about an hour to the action of a small quantity of brown oxyd of lead enclosed in a capsule, and passed up through the mercury into the jar containing the gas. By this means all the sulphureous acid was absorbed, after which the carbonic acid was taken up by dry caustic potash, and no other residue was left than a little common air of the vessels.

In the above analysis therefore the sulphur originally contained in the liquid sulphuret of carbon was procured partly in the form of sulphat of barytes, and partly as sulphureous acid gas. The carbon also was obtained in the form of carbonic acid gas, and the sulphur and carbon added together as nearly equalled the weight of the liquid decomposed as can be ever expected in experiments of this kind. The carbon weighs 15.7 per cent. of the liquid, and the sulphur 84.83.

The data of these computations assumed by Professor Berzelius are, that 100. parts by weight of carbonic acid contain 27. of carbon; that 100 parts of sulphat of barytes contain 13.66 of sulphur, and that 100 parts of sulphureous acid gas contain 51 of sulphur.

Professor Berzelius proceeds to shew how closely this analysis coincides with the law of the combination of combustible bases, which he has laid down in his valuable and elaborate researches (for which see the article *Affinity* in



in this appendix) which law is, that "when two such bodies unite, the proportion in which this combination takes place is such, that if they be oxydated to a certain degree, they will either absorb an equal quantity of oxygen, or one will absorb two, three, four, &c. times as much as the other." In the present instance the oxygen which would convert the sulphur to sulphureous acid would be exactly twice the quantity required to convert the carbon to carbonic acid, provided a slight change were made in the above mentioned numbers expressing the composition of the liquid, making the carbon 15.47 per cent. and the sulphur 81.53.

Carburetted sulphur appears by further experiments to be capable of some degree of combination with alkalies, earths, and metallic oxyds, forming compounds, to which Professor Berzelius proposes to give the name of *Carbo-Sulphurets*.

When a glass bulb with a small orifice filled with liquid carburetted sulphur is introduced into a vessel of ammoniacal gas, a contraction of bulk takes place, and a yellow saline uncrystallized substance is deposited, which contains the whole of the carburetted sulphur saturated with ammonia where the latter abounds. If this substance is sublimed without changing the vessel, it condenses unaltered in a cooler part of the vessel; but the moment it has contact with air it absorbs moisture, and is partially decomposed, and then it gives when sublimed, crystals of hydrosulphuret of ammonia. Carbonic acid is doubtless generated at the same time.

Lime heated in an atmosphere of vaporized liquid carburetted sulphur appears also to contract some union with it, but this compound also is decomposed by moisture.

We shall add a few particulars of Dr. Marcet's experiments on the very intense cold produced by the evaporation of liquid carburetted sulphur.

If the bulb of a small spirit thermometer be closely covered with a bag of fine flannel, or better, with a piece of fine lint, and a few drops of the liquid poured on it, the thermometer (if before at about 60°) rapidly sinks to near 0°.

But if the thermometer bulb thus wetted be introduced into the receiver of an air-pump, and the vessel exhausted, the temperature in one or two minutes will descend from summer heat to -70° or -80, that is about 40 degrees below the freezing point of mercury. Therefore, if instead of a spirit thermometer, a small bulb containing mercury be used, this metal may be

easily frozen, and the phenomena attending its congelation may be seen with great convenience. If the air be very damp this somewhat impedes the experiment.

#### SULPHURIZED MURIATIC ACID.

This singular compound, discovered by Dr. Thomson, has been already described in the *Chim. Dict.* It is considered by Sir H. Davy (agreeably to his theory) as a compound of sulphur and chlorine, and may be immediately prepared by heating a little sulphur in a retort filled with chlorine. The sulphur and the chlorine unite and form a fluid, which distills into the colder part of the retort. It does not redden perfectly dry litmus paper. When agitated with water, much sulphur is deposited, and the water contains muriatic and sulphuric acid.

According to Sir H. Davy's experiments, 10 grains of pure sulphur absorb about 30 cubic inches of chlorine, so that the compound contains by weight 30 parts of sulphur to 67 of chlorine. The compound contains a *maximum* of chlorine, but may be united to an additional portion of sulphur.

This compound has been examined by M. Amadeé Berthollet.\* The general facts found by this able chemist agree with those of Dr. Thomson. When this liquid is shaken with a little water, the mixture acquires very soon a boiling heat, and is rapidly decomposed. The water contains muriatic, sulphureous, and a little sulphuric acid, and sulphur precipitates, which when well washed differs in no respect from common sulphur, and is not (as Dr. Thomson has conjectured) a protoxyd of sulphur. To examine whether the sulphurized muriatic acid contained any sulphureous acid before mixture with water, M. A. Berthollet passed a current of sulphuretted hydrogen through the liquid, but without any apparent decomposition and deposition of sulphur from the gas, which might have been expected had any sulphureous acid been contained. On the other hand, when the gas is received in water it is immediately decomposed, the sulphuretted hydrogen holding in solution a portion of the sulphurized liquor mutually unite, scarcely any of the gas remains uncondensed, sulphur is deposited, and a sensible quantity of sulphuric acid is formed.

When pure dry mercury is shaken with the sulphurized muriatic acid, a very great heat is excited, and the whole is changed to a grey pulverulent mass. This when thrown into water is mostly dissolved, and the solution contains

\* Mem. d'Arcueil, tom. 1.

sulphat and muriat of mercury in a high state of oxydation.

The fact of the acids being only developed when water is added, may be readily explained on Sir H. Davy's theory of the constitution of muriatic acid. If the sulphurized muriatic acid is a mere compound of sulphur and chlorine, water will furnish oxygen to the sulphur, and hydrogen to the chlorine, and thus the sulphur will be acidified, and the chlorine will be changed to muriatic acid.

Professor Berzelius considers this compound as a compound of muriatic acid and *Oxyd of Sulphur*, a substance whose existence is still very hypothetical, as it cannot be produced in any but a compound form: when water is added, the oxyd is decomposed into the sulphur that precipitates, and the sulphureous acid that remains in solution, one portion being oxygenated at the expence of the other. This oxyd of sulphur he considers as being composed of 100 of sulphur to 50 of oxygen, which is half the proportion of oxygen to that in sulphureous acid.

#### SULPHURETTED HYDROGEN. HYDROSULPHURETS.

Some valuable observations on this gas have been made by Sir H. Davy,<sup>a</sup> and by Messrs. Gay Lussac and Thenard.<sup>b</sup> The latter chemists observe, that when this gas is made by digesting the sub-sulphuret of iron with dilute sulphuric acid, the gas is always mixed with a quantity of hydrogen, which is less in the first than in the latter portion obtained. This may be ascertained by shaking the gas in lime-water, which absorbs the sulphuretted hydrogen, and leaves the pure hydrogen. Neither can this gas be prepared pure by heating sulphur in hydrogen gas, as a great portion of the latter always remains unchanged. The best way of obtaining sulphuretted hydrogen is either by digesting sulphuret of antimony in hot concentrated muriatic acid; or by treating the solid hydrosulphurets of potash or soda with a dilute muriatic or sulphuric acid. Care must however be taken that the alkalies are not at the same time partially carbonated, as this would introduce carbonic acid into the gas obtained. Sulphuretted hydrogen contains exactly its own volume of hydrogen, as is proved both by there being no change of bulk when sulphur is heated in hydrogen; and inversely, when the sulphur is extracted from a given portion of sulphuretted hydrogen. This is very conveniently and accurately performed by heating a piece of clean tin in the gas for half an hour at a low red-heat.

All the sulphur is thus extracted, and the remaining gas is pure hydrogen of precisely the same volume as the sulphuretted hydrogen employed. The specific gravity of sulphuretted hydrogen dried by muriat of lime, is given by these chemists as 1.1912 (common air being unity) and hence that of hydrogen being .073199, the composition of sulphuretted hydrogen is 93.855 parts by weight of sulphur, and 6.145 of hydrogen, which is nearly 15 of sulphur to 1 of hydrogen. Sulphuretted hydrogen is soluble in many liquids. Strong muriatic acid will dissolve 3 times its volume at 52°. therm. and 29.92 in. bar. Sulphuric acid diluted with its own weight of water will dissolve  $1\frac{1}{2}$  times its volume at the same pressure and temperature, and water full 3 times. It is necessary for this however that the gas be quite pure, for if mixed with hydrogen the quantity dissolved is much less. When 100 measures of sulphuretted hydrogen are mixed with 50. of oxygen, and exploded by the electric spark, both gasses disappear, water is produced and sulphur deposited: when 150 measures of oxygen are used, the products are about 87 measures of sulphureous acid gas besides the water produced, so that both the component parts are oxygenated.<sup>c</sup>

Sir H. Davy gives as the result of his most accurate observations,<sup>d</sup> that 100 cubic inches of sulphuretted hydrogen at a medium pressure and temperature weigh 56.5 grains, and if it contains its own bulk of hydrogen (of which 100. cubic inches weigh 2.27 grains) it must be composed, by weight, of 2.27 parts of hydrogen, and 34.23 of sulphur, or, in 100. parts, it consists of 6.219 hydrogen, and 93.781 sulphur, which is very exactly 1 of hydrogen to 16 of sulphur. When sulphuretted hydrogen is exposed to common electricity, or if platina wires be ignited in it by the voltaic apparatus, it is rapidly decomposed, sulphur is deposited, and an equal volume of hydrogen remains.

M. Thenard has some observations on the triple compounds of sulphur, sulphuretted hydrogen and a base.<sup>e</sup> When a saturated hydrosulphuret (or a base saturated with sulphuretted hydrogen) is heated with sulphur, a strong effervescence ensues, much of the sulphur is dissolved, and an equivalent portion of the sulphuretted hydrogen escapes in a gaseous form. If on the other hand, the hydrosulphuret is not saturated with sulphuretted hydrogen, when heated with sulphur much of it is still dissolved, but no sulphuretted hydrogen escapes.

The saturated hydrosulphurets when boiled

<sup>a</sup> Elements of Chemistry.

<sup>b</sup> Recherches, tom. i. p. 192.

<sup>c</sup> Dalton.

<sup>d</sup> Phil. Trans. for 1812.

<sup>e</sup> An. Chim. tom. 83. p. 132.

without addition, give out more or less of this sulphuretted hydrogen, and thus are decomposed partially or entirely. The hydro-sulphuret of magnesia is completely decomposed at this heat; that of lime almost entirely; the hydrosulphurets of potash or soda are partially so, and become very alkaline, but still retain so much sulphuretted hydrogen as to give it out abundantly on being heated with sulphur.

The hydrosulphuret of ammonia is deposited in the form of needle-shaped crystals, by passing equal portions of sulphuretted hydrogen and ammoniacal gas into a dry vessel cooled by ice externally. This hydrosulphuret of ammonia is at first colourless, but soon turns yellow when exposed to the air, and then by partial abstraction of the hydrogen contains an excess of sulphur relatively to the hydrogen. It is also very volatile, and sublimes even in a common temperature to the top of the vessel in which it is kept, and thus it may be obtained separate from that portion which has undergone partial decomposition.

The sulphuretted hydrosulphuret of ammonia has an oily consistence when saturated with sulphur, which is effected merely by digesting sulphur with Boyle's fuming liquid (or hydrosulphuret of ammonia) at a common temperature. When this is diluted with water, much sulphur is precipitated, even if liquid ammonia be previously added. This saturated sulphuretted hydrosulphuret of ammonia gives out vapours in the air, but much less than Boyle's liquid; which latter will give out a very dense vapour for a long time when exposed to oxygen, but scarcely any in azote or hydrogen.

#### SULPHUREOUS ACID.

When sulphur is burnt in a given quantity of dry oxygen gas, the sole product is sulphureous acid gas. Some condensation always takes place, but it is variable, and in small quantity when the sulphur is the purest. It therefore is most probably owing to some hydrogen remaining in the sulphur, so that if sulphur were quite pure, it would probably be converted into sulphureous acid gas by oxygen without any change of bulk. Therefore, by ascertaining the weight of a given volume of sulphureous acid gas, and deducting from it the weight of an equal bulk of oxygen the remainder will be the sulphur. Thus 100 cubic inches of sulphureous acid gas weigh at a mean pressure and temperature 68 grains, and 100 cubic inches of oxygen gas weigh 34 grains, leaving also 34 for the weight of the sulphur. Hence it is most probable that sulphureous acid

gas is composed of equal weights of sulphur and oxygen, and the absolute weight of each in a given quantity of the acid gas, is equal to that of the same volume of oxygen.

Another proof of the constitution of sulphureous acid is obtained from the combustion of sulphuretted hydrogen in Volta's eudiometer.\* This compound contains exactly its own bulk of hydrogen, and 100. cubic inches consist (as above mentioned) of 34.23 grains of sulphur, and 2.27 grains of hydrogen. Now when sulphuretted hydrogen is exploded with abundance of oxygen, the products are sulphureous acid gas and water; and 2 measures of sulphuretted hydrogen require 3 measures of oxygen for this purpose, or 100. require 150. of oxygen. Therefore, according to the well known constitution of water, the 100. cubic inches of hydrogen (contained in the same bulk of sulphuretted hydrogen) require 50. cubic inches of oxygen to produce water, which would leave 100. cubic inches of oxygen, weighing about 34. grains, to form sulphureous acid with 34.23 grains of sulphur, which are nearly equal weights.

Professor Berzelius ascertains the composition of sulphureous acid from the sulphate of barytes, as mentioned in the article *Affinity* in this appendix, which gives the component parts of this acid to be 100. of sulphur, and 97.83 oxygen. These differ but little from being equal parts of each.

#### SULPHURIC ACID.

Much information has been lately given by experimental researches on the constitution of this most important acid, and the theory of its formation. It has long been known that the most concentrated acid which can be obtained in a separate state, contains a considerable quantity of water in its composition, which may be expelled when it enters into chemical union with any base, a fixed alkali for example, and it is on this principle that Mr. Kirwan formed his tables for the proportions of real acid in liquid sulphuric acid of different degrees of dilution. Sulphuric acid therefore is composed of sulphur, oxygen, and water, the latter of which it is capable of giving up when it enters into combination with a base.

The proportion of oxygen to sulphur in sulphuric acid appears by a variety of experiments to be  $1\frac{1}{2}$  times as much as that in sulphureous acid, and in the latter it is as already mentioned, nearly, if not exactly, equal to the sulphur. So that if 30 grains of sulphur take 30 grains of oxygen to become sulphureous acid, it will

\* Dalton's System, vol. ii.

require 45 grains of oxygen to form dry sulphuric acid such as exists in the neutral sulphats after ignition. Sir H. Davy estimates the water in 100 parts of the most concentrated liquid sulphuric acid to be about 19 in 100, and hence the composition of liquid sulphuric acid in 92 parts will be as follows :

Sulphur . . . 30	}	75	Dry sulphuric acid:
Oxygen . . . 45			
Hydrogen . . . 2	}	17	Water
Oxygen . . . 15			

92 Liquid sulphuric acid

If this be correct, the sulphur will unite with three portions of oxygen (45) to produce the acid, and this with one portion of oxygen (15) in the water essential to its separate state, which will agree with the opinion advanced by Berzelius, that the oxygen of the water in definite compounds is an equal portion of that in the other constituents. (*See Affinity in this appendix.*) Since sulphureous acid consists of sulphur with two portions of oxygen, and sulphuric acid, of sulphur with three portions, and since sulphureous acid gas occupies the same space as its oxygen alone would fill, it must therefore follow that whenever sulphuric acid is partially decomposed, it will resolve itself into two parts in volume of sulphureous acid gas, and one volume of oxygen gas. This is actually found to be the case by experiment: for when the strongest sulphuric acid is vaporized by heat, and in this state passed through a red-hot porcelain tube, it is resolved into a gas consisting of two volumes of sulphureous acid and one volume of oxygen, and a liquid condenses, which is the same as dilute sulphuric acid. It would appear therefore in this experiment that only a portion of the acid is decomposed, but none of the water.

When a solution of sulphureous acid gas recently made, is heated, nearly if not entirely the whole of the gas may be again expelled by long boiling; but if it be exposed to the air for some time, it loses its peculiar smell, becomes strongly sour, and is converted into a weak solution of sulphuric acid, which may be concentrated by evaporation.

The experiments of Professor Berzelius (*see Affinity in this appendix*) very nearly agree with the composition of sulphuric acid above mentioned. He shews that the sulphuret of lead is totally converted into neutral sulphat of lead by the action of nitric acid, that is to say by the addition of oxygen, and therefore that

the sulphur and the lead are in the same relative proportions to each other in both preparations. Hence by previously ascertaining the quantity of oxygen contained in the suboxyd of lead, which is the base of the sulphat, and by finding the total addition of oxygen required to convert the sulphuret into sulphat, the oxygen required by the sulphur alone to produce the sulphuric acid of the sulphat is readily found. This gives the composition of dry sulphuric acid to be 39.92 of sulphur to 60.02 of oxygen, or almost exactly 2 parts of sulphur to 3 of oxygen, which agrees as nearly as can be expected with the proportions before given.

A very instructive memoir on the decomposition of the metallic sulphats by heat, is given by M. Gay Lussac.<sup>a</sup> All these salts are decomposable by a heat more or less intense, but the products of this operation vary according to the force of the affinity of the metals for sulphuric acid. The soluble sulphats in which the acid is but little condensed, give only sulphuric acid by distillation. But those that retain the acid strongly, and are at the same time insoluble, give out their acid decomposed into sulphureous acid and oxygen gasses: and the sulphats that are acid and soluble, but yet retain the acid with considerable force, give out their acid when heated, partly as sulphuric acid, and partly as sulphureous acid and oxygen. Some of the experiments are as follows. Sulphat of copper was distilled in an earthen retort in a furnace capable of giving a very intense heat. It had been previously calcined to expell the water. The products were a most abundant stream of mixed gas, which continued for an hour without abatement. On encreasing the heat the gas again appeared, and different portions of it were reserved for analysis. At the last the heat was urged with great violence as long as any thing was given out. The copper was found reduced and fused in a button at the bottom of the vessel. On examining the gas obtained at different periods of the distillation, it was found to consist very uniformly of about 32.5 per cent. (in volume) of oxygen and the rest sulphureous acid, except the last portion of all, which contained as much as 92.4 of oxygen, and was obviously produced at the time of the reduction of the oxyd of copper in the extreme heat. Therefore (setting aside the last portion) it appears that in the sulphat of copper, the sulphuric acid soon begins to be decomposed when heated, and continues this change uniformly as long as any acid remains.

<sup>a</sup> Mem. d'Arcueil, tom. 1.

The same was observed from alum strongly heated, the gas being a pretty uniform mixture of about two parts in volume of sulphureous acid, and one part of oxygen, and this continued without change to the end of the process, as the base of this sulphat was not itself deoxygenated by the heat.

Sulphat of iron has long been employed to yield sulphuric acid by its distillation, but besides the sulphuric, it also gives out much sulphureous acid gas. This was long supposed to arise from the higher degree of oxygenation which the metal acquires in the process, (which is actually the case) but it was observed by Chaptal that oxygen gas was also given out, and hence only a portion of the acid of this salt is obtainable by distillation unchanged, and the rest appears in the form of sulphureous acid and oxygen, as in the distillation of sulphat of copper.

The sulphats of manganese and zinc also give out most of their acid decomposed.

When sulphuric acid is digested on tin, antimony or bismuth, two sulphats are formed, one, very soluble, and with a great excess of oxyd; the other, little soluble, and with excess of oxyd. The former of these yields much of its acid unaltered in distillation; the latter gives it out in the form of its constituent parts, oxygen and sulphureous acid.

The sulphat of silver, which is one of the insoluble sulphats that retains its acid strongly, gave out its acid decomposed, and the metal was reduced.

Sulphat of mercury underwent a similar change.

With regard to the sulphats of the fixed alkalis and of some of the earths, they are undecomposable by distillation *per se* when neutral; but of some of the acid sulphats so much of the acid is decomposed as constitutes the excess beyond the point of neutralization. Thus the acid sulphat of potash gives out, on heating, part of its acid unchanged, and part in the form of sulphureous acid and oxygen, till it is brought to the neutral sulphat, when no further change occurs.

But even the neutral sulphats will be partially decomposed, when distilled with vitreous phosphoric or boracic acid; and the products therefore will be, not sulphuric acid, but its elements, sulphureous acid and oxygen.

The theory of the formation of sulphuric acid by the combustion of sulphur and nitre, as now so generally practised, has been the subject

of much controversy. The common opinion that the nitre acts merely by furnishing oxygen to the sulphur, is fully confuted by the fact that sulphur burnt in oxygen gas does not produce sulphuric acid, but only a mixture of sulphureous acid gas and oxygen; and also, that the quantity of nitre found sufficient for the purpose would not furnish nearly enough oxygen to the sulphur.

Some interesting remarks on this subject are given by Messrs. Desormes and Clement.<sup>b</sup> These chemists shew that even when the nitre is one fifth of the sulphur (which is the largest allowance) it will not furnish one fifth enough oxygen to acidify the sulphur; and the sulphat of potash alone which remains in the residue contains as much oxygen as all the nitre.

They observe that when the mixture of nitre and sulphur is burning in the pots of the leaden chamber in which sulphuric acid is made, the nitric acid is obviously not entirely decomposed, for much red nitrous acid vapour is diffused in the chamber along with the sulphureous acid. The combustion of the mixture in the pots therefore first produces a mixture of nitrous acid gas and sulphureous acid gas, together with the vapour of water, but these acid gasses cannot subsist together for a moment (when moist) without mutual decomposition into sulphuric acid and nitrous gas, which therefore happens in the body and upper part of the chamber. A condensation of the sulphuric acid vapour then takes place, which is absorbed by the water on the floor. This forms a partial vacuum, that is filled by external atmospherical air, which last is in its turn decomposed by the nitrous gas absorbing its oxygen and becoming nitrous acid gas. This again is ready to furnish oxygen to a fresh portion of sulphureous acid gas diffused in the chamber, which again produces sulphuric acid that condenses in the water below, and nitrous gas, and occasions a vacuum supplied from the air from without; and the gas, now become nitrous acid gas, continues as before to complete the oxygenation of fresh portions of sulphureous acid.

The nitric acid therefore is constantly in a state of successive decomposition and recomposition by the successive portions of oxygen which it furnishes to the sulphureous acid, and again by the re-absorption from the air of the oxygen which it thus loses. These changes are very well shewn by introducing into a large open glass globe first a quantity of sul-

<sup>b</sup> An. Chim. tom. 59.

phureous acid gas, then adding a small quantity (about  $\frac{1}{20}$ ) of nitrous gas, which will immediately produce red fumes of nitrous acid gas, followed by a white dense vapour which gradually condenses on the inner surface of the glass in shining stellated crystals, and the air of the vessel again becomes transparent. If a few drops of water are then introduced, the crystals dissolve with great heat, and the nitrous gas is again expelled, which directly changes as before into red nitrous acid vapour, and the same round of chemical action goes on till all the oxygen of the air in the vessel is exhausted, or till all the sulphureous acid gas is consumed.

The presence of water is essential to the formation of sulphuric acid, for if sulphureous acid gas and nitrous acid gas both perfectly dry be brought in contact, no action ensues: but

the least portion of moisture causes them to condense into the solid crystalline compound above described; and a little more water generates liquid sulphuric acid, and the nitrous gas is expelled. Sometimes, in making the above experiment, the decomposition of the nitrous acid gas proceeds further than the generation of nitrous gas, and produces nitrous oxyd. It does not appear precisely what is the reason of this variety of effect; but when it does occur it stops the further acidification of the sulphureous acid, as the nitrous oxyd will not spontaneously reabsorb from the air the oxygen which it has lost.

We shall now give Mr. Dalton's table of the strength of sulphuric acid at different densities, the results of his own experience in this acid for several years. <sup>c</sup>

Table of the quantity of real acid in 100. parts of liquid sulphuric acid, at the temperature of 60°.

Acid per cent. by weight.	Acid per cent. by measure.	Specific gravity.	Boiling point.
100	unknown	unknown	unknown
81	150	1.850	620°
80	148	1.849	605°
79	146	1.848	590°
78	144	1.847	575°
77	142	1.845	560°
76	140	1.842	545°
75	138	1.838	530°
74	135	1.833	515°
73	133	1.827	501°
72	131	1.819	487°
71	129	1.810	473°
70	126	1.801	460°
69	124	1.791	447°
68	121	1.780	435°
67	118	1.769	422°
66	116	1.757	410°
65	113	1.744	400°
64	111	1.730	391°
63	108	1.715	382°
62	105	1.699	374°
61	103	1.684	367°
60	100	1.670	360°
58.6	97	1.650	350°
50	76	1.520	290°
40	56	1.408	260°
30	39	1.30+	240°
20	24	1.200	224°
10	11	1.10—	218°

<sup>c</sup> New System.

In the above table the first line is a substance which probably does not exist, being the pure acid, supposed to be in a liquid state and free from all water. It is composed of single atoms of sulphuric acid, and the relative weight of each atom is given by Mr. D. to be 34 times that of an atom of hydrogen. This number is derived from the assumed composition of an atom of sulphuric acid to be one atom of sulphur (13) with 3 of oxygen (21). The atom of sulphur again is derived from the actual composition of sulphureous acid, which is estimated at 48 parts by weight of sulphur and 52 oxygen; and it is assumed to consist of 2 atoms of oxygen (14) to 1 of sulphur and 52:48::14:13 which gives the relative weight of the atom of sulphur to be 13. (hydrogen being always unity.)

But on the other hand, if sulphureous acid consists of equal weights of sulphur and oxygen, the atom of sulphur will be 14. and the atom of sulphuric acid will be  $14 + 21 = 35$ , being 1 atom of sulphur and 3 of oxygen.

Mr. Dalton infers that the acid of 81. per cent. by weight, or 1.85 specific gravity, is composed of an atom of real sulphuric acid and an atom of water. This is nearly the mean of each estimation of the atom of sulphuric acid, for if it is taken at 34. an atom of this and an atom of water would indicate a strength of 81.4 per cent. of real acid; and if it is taken at 35. it will indicate 80.95 per cent. As this acid of 1.85 specific gravity is the strongest liquid sulphuric acid that can be procured in an uncombined state, and distills unchanged without becoming more concentrated, and is a well defined specific compound, there is great reason to suppose it to consist of some simple definite proportion of acid and water.

The next definite compound of sulphuric acid and water, according to Mr. Dalton's system, will be that which is composed of 1 atom of real acid and 2 atoms of water, and this forms the acid of 68. per cent., by weight, of acid and 1.78 specific gravity. It is worthy of remark that this is the acid which Mr. Keir has discovered to possess the remarkable property of congealing at 32° and remaining unthawed at any temperature below 46°, as we noticed in our former article of *Sulphuric Acid* (*Chem. Dict.*) If the acid be as little as 1 per cent. stronger or weaker, this remarkable property of remaining congealed at a comparatively high temperature is lost.

No peculiar properties have hitherto been

discovered in any other of the definite points of dilution of the acid. The acid of 58.6 per cent., by weight, of real acid contains by Mr. Dalton's estimation 1 atom of acid to 3 atoms of water; that of 30 per cent. contains 1 atom of acid to 10 of water; that of 20 per cent. contains 1 of acid to 17 of water; and that of 10 per cent. contains 1 of acid to 38 of water.

Mr. Dalton's table differs considerably from that of Mr. Kirwan. As the specific gravity increases but little in proportion to the strength of the acid in the more concentrated mixtures, Mr. Dalton observes, that in these it is safer for practical utility to depend on the temperature at which the acids boil to form a ready estimate of their strength, as this gives a greater range for examination.

We shall conclude this article with a table of the strength of different mixtures of sulphuric acid and water drawn up for practical purposes of M. Vauquelin, from experiments made with great care.<sup>a</sup> This table may be of service to the English chemist, though it is chiefly calculated for an instrument (Beaume's areometer) which is but little employed in this country, and of no precise authority. M. Vauquelin's table would have been perhaps rather more useful if the standard or concentrated acid which he employed had been somewhat stronger; for as it is, it wants much of the strength of the most concentrated acid, and is somewhat lower than the strong sulphuric acid usually sold in this country. As this eminent chemist asserts that the experiments were most carefully made, no doubt can be entertained of their accuracy.

Table of the proportions (by weight) of standard sulphuric acid of 1.842 specific gravity and of water, in 100. parts of sulphuric acid of different degrees of dilution—Temperature, 12°. Reaumur. = 59°. Fahr.

Beaume's Areometer.	Specific Gravity.	Standard Acid.	Water.
66.	— 1.842	— 100.00	— 0.
60.	— 1.725	— 84.22	— 15.78
55.	— 1.618	— 74.32	— 25.68
50.	— 1.524	— 66.45	— 33.55
45.	— 1.466	— 58.02	— 41.98
40.	— 1.375	— 50.41	— 49.59
35.	— 1.315	— 43.21	— 56.79
30.	— 1.260	— 36.52	— 63.48
25.	— 1.210	— 30.12	— 69.88
20.	— 1.162	— 24.01	— 75.99
15.	— 1.114	— 17.39	— 82.61
10.	— 1.076	— 11.73	— 88.27
5.	— 1.023	— 6.60	— 93.40

<sup>a</sup> Ann. Chim. tom. 76. p. 260.

SULPHATS, *Alkaline and Earthy.*

The manufacture of sulphat of magnesia or Epsom salt, as practised at Lymington in Hampshire, is thus described by Dr. Henry,<sup>a</sup> on the authority of Mr. St. Barbe the proprietor. Seawater, concentrated by spontaneous evaporation in the air, is boiled down to dryness in pans, and the mass is taken out entire and removed into troughs with holes at the bottom, where the mother liquor drains through, leaving the muriat of soda nearly pure. The Epsom salt is made from this mother liquor in the winter season, by a very simple process. The mother liquor is boiled for some hours in the salt pans, and the impurities are removed by skimming. During the evaporation a portion of common salt separates, which is removed. The evaporated liquor is then poured into wooden coolers 8 feet long, 5 wide and 1 foot deep. In these it remains twenty-four hours, during which time, if the weather prove clear and cold, the sulphat of magnesia crystallizes at the bottom of the cooler in quantity equal to about one-eighth of the boiled liquor. The uncrystallizable fluid is then let off through plug-holes at the bottom of the coolers; and the Epsom salt is drained in baskets. This is termed *single* Epsom salt, and after a second solution and crystallization it is termed *double* Epsom salt. Four or five tons of sulphat of magnesia are obtained from a quantity of brine which has yielded 100 tons of common salt.

*Sulphat of Barytes.* Many of the methods of decomposing this salt have been already mentioned; the following is given by Goettling.<sup>b</sup> Mix together in fine powder eight parts of native sulphat of barytes, two parts of muriat of soda, and one part of charcoal powder. Press the mixture hard into a Hessian crucible, and expose it for an hour and a half to a red heat in a wind furnace. When cold, reduce the mass to powder and boil it for a short time in sixteen parts of water; filter the lixivium and keep it in well stopped bottles. To prepare muriat of barytes from this lixivium, add muriatic acid as long as any sulphuretted hydrogen gas is extricated. Evaporate the liquid to a pellicle, and set it by to crystallize, when the muriat of barytes will separate. Again evaporate the liquid part, removing the muriat of soda that forms in the process, and by cooling, a fresh portion of muriat of barytes will crystallize.

The composition of some of the sulphats is thus given by Berzelius.<sup>c</sup>

*Sulphat of Barytes* is thus found: 100 parts

of carbonat of barytes contain 77.904 barytes, and produce 118.6 sulphat of barytes. Hence the composition of this latter salt is

Sulphuric acid 34.314 — 100.000  
Barytes . . . 65.686 — 191.427

*Sulphat of Potash.* 100 parts of ignited sulphat of potash give 134.68 of sulphat of barytes, hence it consists of

Sulphuric acid 46.214 — 100.000  
Potash . . . 53.786 — 116.385

Sulphat of potash when crystallized contains no more than about 1. of water in 300 of the salt.

*Sulphat of Soda.* 100 parts of ignited sulphat of soda give 164 sulphat of barytes, hence it consists of

Sulphuric acid 56.275 — 100.000  
Soda . . . 43.725 — 77.699

*Sulphat of Magnesia.* 100 parts of ignited sulphat of magnesia give 194.3 of sulphat of barytes; hence this salt consists of

Sulphuric acid 66.64 — 100.00  
Magnesia . . 33.36 — 50.06

*Sulphat of Ammonia.* This salt was analyzed by distillation with lime, and gave 53.1 of sulphuric acid, 22.6 of ammonia, and 24.3 of water of crystallization. Hence (excluding the water) this salt consists of

Sulphuric acid 70.14 — 100.000  
Ammonia . . 29.86 — 42.617

SULPHURETS. *Metallic.*

M. Vauquelin has given the results of some experiments, to determine the proportions of sulphur which several metals absorb by fusion. These proportions have been variously stated by different chemists, chiefly owing to a difference in the heat employed, and the mode of its application. In these experiments M. Vauquelin states, that the heat was kept up to a degree sufficient to melt the compounds, and long enough to expell all the superabundant sulphur. The contact of the external air was also avoided. Each experiment was repeated three or four times, and those results were rejected which differed from the majority by more than two hundredth parts. The metals were divided as much as possible, and mixed with thrice their weight of sulphur, and also covered with a layer of sulphur. The sulphurets that required considerable heat for fusion, such as those of iron and copper, were three times successively pulverized and treated with fresh sulphur, to ensure a perfect saturation.

<sup>a</sup> Phil. Trans. 1810. p. 94.

<sup>b</sup> Phil. Journ. vol. ii. p. 161.

<sup>c</sup> Ann. Chim.



The following are the results:

*Sulphuret of Copper.*

Copper	-	78.69
Sulphur	-	21.31
		<hr/>
		100.00

*Sulphuret of Tin.*

Tin	-	85.9
Sulphur	-	14.1
		<hr/>
		100.0

*Sulphuret of Lead.*

Lead	-	86.23
Sulphur	-	13.77
		<hr/>
		100.00

*Sulphuret of Silver.*

Silver	-	87.27
Sulphur	-	12.73
		<hr/>
		100.00

*Sulphuret of Iron.*

Iron	-	78.
Sulphur	-	22.
		<hr/>
		100.

*Sulphuret of Antimony.*

Antimony	-	75.
Sulphur	-	25.
		<hr/>
		100.

*Sulphuret of Bismuth.*

Bismuth	-	68.25
Sulphur	-	31.75
		<hr/>
		100.00

*Sulphuret of Manganese.*

Manganese	-	74.5
Sulphur	-	25.5
		<hr/>
		100.0

*Sulphuret of Arsenic.*

Arsenic	-	57
Sulphur	-	43
		<hr/>
		100

The sulphuret of manganese is the only one of these combinations which was not made directly from the metal, but instead of it, the dry carbonat of manganese was employed, which, after fusion with sulphur, gave a green spongy mass resembling the native sulphuret, and gave abundance of sulphuretted hydrogen by dilute nitric acid. M. Vauquelin reckons the quantity of sulphur in this sulphuret to be at least equal to the loss of weight which the dry carbonat would undergo by ignition *per se*; in which case the manganese in this sulphuret will be in the state of sub-oxyd. If, however, it passes to the reguline state by fusion with sulphur, the proportion of the latter substance must be greater than is here stated, by the weight of the oxygen supposed to remain.

Most of these proportions here given agree pretty nearly with those of Proust, and also of Berzelius, with the exception of iron. M. Vauquelin accounts for the difference between his and Proust's estimation of the sulphur in the sulphuret of iron, by the different circumstances of the respective experiments, the latter chemist having employed a much lower temperature. But the artificial sulphurets of iron prepared by Proust, agree very nearly in composition with the two natural sulphurets analyzed by Mr. Hatchett, viz. the magnetical, and the common pyrites, as we have fully related in the *Chem. Dict. Art. Iron*. These apparent inaccuracies are readily reconciled, by supposing each of these sulphurets to exist in definite proportions, that of Vauquelin being in the lowest known degree of sulphuration. This will also account for the intermediate sulphuret, between the magnetical and the common pyrites, actually obtained by Mr. Hatchett, by distilling the magnetical pyrites with sulphur in a low red-heat short of fusion, the existence of which is assumed hypothetically by Berzelius, as the base of the red sulphat of iron.

The four sulphurets of iron thus obtained, will therefore be composed as follows, taking M. Vauquelin's experiment as the basis of the calculation, and encreasing the sulphur in this sulphuret by the simple ratios of 2, 3, and 4 times 28.21.

*First Sulphuret (artificial).*

Iron	78	—	100.00
Sulphur	22	—	28.21

*Second Sulphuret (natural)  
Magnetical Pyrites.*

Iron	63.93	—	100.00
Sulphur	36.07	—	56.42

*Third Sulphuret (artificial).*

Iron	54.16	—	100.00
Sulphur	45.84	—	84.63

*Fourth Sulphuret (natural)  
Common Pyrites.*

Iron	46.98	—	100.00
Sulphur	53.02	—	112.84

See Article AFFINITY and IRON, in this Appendix.

## T

## TABULAR SPAR.

The colour of this mineral is greyish white, passing more or less into greenish, yellowish, and redish. Its structure is lamellar in one direction, but on a near examination joints may be observed parallel to the sides of a slightly rhomboidal prism, with further indications of joints parallel to the two diagonals. These lamellæ are often aggregated into coarsely fibrous or prismatic distinct concretions. The lustre of the recent fracture is shining and pearly. It is translucent and moderately hard. Sp. gr. 2.86. When scratched by a point of iron in the dark it becomes phosphorescent. When thrown into nitric acid it makes a momentary effervescence and then divides into grains. It is composed, according to Klaproth, of

50. Silix
45. Lime
5. Water
<hr/>
100.

It has been found only at Dognatska in the Bannat, where it occurs in a vein mixed with bluish lamellar calcareous spar with green garnets.

## TOPAZ.

The mineral described by Werner under the

name of Schorlaceous Beryl, and by Haiiy under that of Pycnite, has recently been discovered to bear a very striking analogy to topaz. Its characters in brief are the following. Hardness, somewhat superior to that of quartz; colour, yellowish, greenish and redish-white, more or less translucent. It occurs either massive composed of parallel prismatic concretions with transverse rents, or crystallized in long hexahedral prisms. Cross fracture imperfectly foliated; longitudinal fracture imperfectly conchoidal, with a glistening resinous lustre: fragile. Sp. gr. 3.5

Not electric by heat; infusible before the blowpipe. Has been analyzed by Klaproth and Vauquelin with the following results.

K.	—	V.
43.	—	30. Silix
49.5	—	60. Alumine
0.	—	2. Lime
4.	—	6. Fluoric acid
1.	—	1. Water
1.	—	0. Oxyd of iron
<hr/>		<hr/>
98.5		99.

It occurs in Saxony, Bohemia, and Moravia, imbedded in gneiss, or in a rock composed of quartz and mica.

## U

## ULMIN.

This name has been given by Dr. Thomson, to a peculiar gum-like matter, found occasionally on the trunk of the elm tree, which was first obscurely noticed by Vauquelin, as contained in a morbid juice flowing from the tree;<sup>a</sup> and afterwards more fully analyzed by Klaproth,<sup>b</sup> as composing a solid matter sent to this eminent chemist from Palermo. A substance almost exactly similar, collected from an elm-tree at Plymouth, has since been analyzed by Dr. Thomson;<sup>c</sup> and still more recently, a portion of the

same sample that was examined by Klaproth, has been analyzed by Mr. Smithson.<sup>d</sup> All these so nearly agree in their results, that the same description will serve for all.

Ulmin is a bright, hard, black substance, breaking with a vitreous fracture. It is nearly tasteless. When heated it does not melt, but swells very much. It readily burns at the flame of a candle, or in an open crucible, and leaves a white alkaline ash, consisting chiefly of subcarbonat of potash, of which the potash alone, according to Mr. Smithson, is about a

<sup>a</sup> Ann. Chim. tom. 21.

<sup>b</sup> Thomson's Annals, No. 1.

<sup>c</sup> Ibid.

<sup>d</sup> Phil. Trans. 1813.

fifth of the weight of the ulmin employed. Notwithstanding this great proportion of alkali, the solution of ulmin itself shews little if any traces of free alkali by its effects on vegetable colours, so that the alkali must be under some form of combination which masks its peculiar characters, though the nature of this combination is unknown. In this respect however it agrees with all other vegetable matter, yielding an alkaline ash; but what is remarkable is the ready formation of nitrat or muriat of potash, by adding these acids to the watery solution of ulmin. Ulmin dissolves readily and copiously in water, and the solution, when evaporated to dryness, is equally again soluble in water. But neither alcohol nor ether have any action on ulmin, and in this respect it differs from vegetable extract, which readily dissolves in alcohol. The watery solution of ulmin is not disturbed by solution of isinglass, by tincture of galls, or by prussiat of potash. Green sulphat of iron gives a copious muddy brown precipitate. The same effect is produced by muriat of tin, nitrat of mercury, and superacetate of lead. Common spirit of wine does not disturb the watery solution, but pure alcohol separates the ulmin almost totally, according to Klaproth.

Another remarkable character of ulmin is this: when nitric or muriatic acid is poured into the watery solution, a copious precipitate, resembling a resin, falls down, and the liquor affords, on evaporation, nitrat or muriat of potash, according to the acid used, as already mentioned. This resin-like substance differs from the entire ulmin in being soluble in alcohol as well as in water, but in each sparingly. The solution in water is much helped by the addition of alkali, and the liquor then closely resembles the original ulmin.

When nitric acid is added to a watery solution of ulmin, and the resinous matter thence produced is separated by the filter, the remaining liquid, when evaporated, furnishes a yellow matter that deflagrates vividly when heated to from 300° to 400° Fahr. owing to the intimate combination of the nitre, with either a portion of the resin remaining in solution, or with some other combustible matter not separable by this acid. Ulmin is therefore composed, of potash, of a peculiar resin-like or rather extractive matter, and probably of some other vegetable principle which has hitherto not been produced in its separate state.

#### URINE. UREA. URIC ACID.

The greater part of the extract of healthy urine consists of *Urea*, which is separated (as mentioned under the article *Urine, Ch. Dict. vol. 2.*) in the form of light pearly scales like boracic acid, on the addition of a little nitric acid.

But in that singular disease, the diabetes mellitus, the urea disappears more or less completely, and a true saccharine matter takes its place in the extract of urine. It is of some importance to be able to find the relative proportions of urea and saccharine matter at the time when this disease is not fully formed, or when it is giving way to particular modes of treatment.

Dr. Henry has given some experiments on this point,<sup>a</sup> by making artificial mixtures of different proportions of diabetic sugar and extract from healthy urine, and he finds that this separation of scaly crystals of urea, on adding nitric acid, does not appear even after standing many hours, where the sugar is six times the quantity of the extract.

But though the urea under these circumstances, cannot be obtained in a separate state, its existence may be proved, and even its proportion estimated, with tolerable accuracy, by the quantity of carbonat of ammonia which the extract of urine will yield when distilled by a boiling-water heat; for Messrs. Fourcroy and Vauquelin have shewn, that urea is the only animal matter hitherto known, which can be decomposed and yield ammonia at so low a temperature; and nearly the whole of this alkali, produced from urine, is to be attributed to decomposed urea. Hence it is that manufacturers, who distill urine for the ammonia, find that fresh urine yields as much of this alkali as when putrid.

*Uric Acid.* A memoir has been published on this acid by Dr. Henry,<sup>b</sup> who has given a full account of its distinguishing properties and its saline compounds. Dr. H. obtained it from that species of urinary calculus which is composed chiefly of this acid. To obtain it, let the calculus, finely powdered, be dissolved in a heated solution of pure potash, supersaturate the liquid with muriatic acid, and the uric acid will fall down in white shining plates, which must be repeatedly washed with distilled water with a little carbonat of ammonia added to the first washings, and dried at a heat not exceeding boiling water. This acid will redden litmus,

<sup>a</sup> Medico-Chirurgical Trans. vol. 2.

<sup>b</sup> Manchester Trans. vol. 2. second series.

but has no sour taste. It unites with the pure alkalies and saturates them, but will not expell the carbonic acid from the carbonated alkalies. When a little of this uric acid is heated on a bit of glass, with a few drops of nitric acid, and evaporated to dryness, the residuum has a beautiful red colour, which stains animal and vegetable matter. This colour is destroyed by acids and pure alkalies, and is not restored by any known re-agent. This singular property of reddening when heated with nitric acid, is quite characteristic of *Uric Acid*, but, as the author asserts, does not belong to *Urea*. The uric acid, when digested in substance with a

solution of soap, is more copiously dissolved than it could be in water alone, and in this degree of concentration it decomposes the soap, separating part of the oil, and forming a kind of emulsion with the rest and the alkali.

Caustic potash copiously dissolves uric acid, but this solution is decomposed by all acids, even the carbonic, and by carbonat of ammonia. Where less acid is used than will saturate all the alkali, an insoluble urate of potash falls down, but where an excess of the precipitating acid is used, the uric acid separates singly. The urates are all insipid and little soluble.

## W

WAVELLITE. <sup>a</sup> Hydrargillite.

This substance occurs in fibres or acicular four-sided prisms, sometimes aggregated into stalactitical masses, but more usually diverging from a common centre, and either separated or adhering to each other by their sides, composing hemispherical concretions of various sizes up to the bulk of a small hazel-nut. The colour is greyish greenish or yellowish white, and often superficially an ochery brown. Its lustre is silky; it is more or less translucent, and is harder than calcareous spar. Sp. gr. about 2.7.

It is infusible *per se*, but by a strong heat becomes white and opaque. It is readily melted by the assistance of borax.

By an intense heat it gives out nearly 30 per cent. of a somewhat empyreumatic and slightly acidulous water. It is composed, according to Sir H. Davy, of

70.	Alumine
1.4	Lime
26.2	Water
<hr/>	
97.6	
2.4	loss
<hr/>	

Subsequent examination has since detected in it a portion of fluoric acid.

It was first discovered by Dr. Wavel, lining the joints and forming veins in a soft argillaceous slate near Barnstaple in Devonshire: it was next found by Mr. Gregor, adhering to quartz crystals, and resembling zeolite, in a mine called Stenna Gwyn in Cornwall. It has also since been discovered in Ireland near the town of Cork; and the stalactitical variety has been brought from Brazil by Mr. Mawe.

WINE. See ALCOHOL.

## Z

## ZINC.

It has been mentioned in our former article that zinc, though but imperfectly malleable when cold, is very completely so when heated from 210° to 300°, so as to allow of its being beaten out or laminated into very thin plates and drawn out into fine wire. It appears too that the zinc after having been thus wrought, does not return to its former brittleness; and hence it may be employed with equal ease as lead or copper for plating, sheathing, roofing, &c. Laminated zinc does not readily rust in the air beyond the first thin hard coating of oxyd, which protects the metal beneath from

the further action of the air. This mode of rendering zinc malleable was first employed in this country by Messrs. Hobson and Silvester of Sheffield.

*Oxydation of Zinc.* It is not well ascertained whether there is more than one oxyd of zinc, which is the white flocculent oxyd that rises from the combustion of this metal; and is also the same that enters into the composition of all the salts of this metal. Proust gives the composition of this oxyd to be 80 of metal and 20 of oxygen. Berzelius<sup>b</sup> found that 10. parts of distilled zinc dissolved in nitric acid and the solution evaporated and ignited, encreased to

<sup>a</sup> Phil. Trans. 1805.

<sup>b</sup> An. Chim. tom. 81. p. 24.

12.44, which therefore gives for the composition of the oxyd

Zinc	80.39	—	100.0
Oxygen	19.61	—	24.4
	<u>100.00</u>		<u>124.4</u>

This agrees very nearly with Proust.

When zinc is burned in chlorine (oxymuriatic gas) a gray solid semitransparent substance is

formed, usually called *butter of zinc*, (*zincane* of Davy).<sup>c</sup> It is also produced by heating together zinc filings and corrosive sublimate. This has a waxy consistence, fuses at about 212°. and is sublimed at less than a red heat. It is composed of equal parts by weight of zinc and chlorine.

Zinc readily alloys with potassium and sodium.

<sup>c</sup> Elements.

## ADDENDUM.

### IODINE.

A new and very singular substance has lately been discovered in France by M. Courtois, and a general sketch of its properties has been given in the *Moniteur* for the 12th of December last. A translation of this paper, with some facts relative to the preparation of this substance by Dr. Thomson, is inserted in No. 14 of the *Annals of Philosophy*, from which this account is chiefly extracted.

The substance in question, *Iodine*, is prepared from kelp by a very simple process. The kelp is lixiviated with water, and the solution evaporated to dryness. This dry salt is put into a tubulated retort, with a short neck fitting into a large globular glass receiver, leaving room for the air to escape: strong sulphuric acid is poured on the salt through the tubulure of the retort, a violent effervescence ensues, and a violet coloured gas is driven off in abundance, which condenses on the receiver into shining crystallized spiculæ of a metallic appearance, somewhat resembling very fine plumbago. This substance is *Iodine*, so called from the *violet* colour (*iadns*) which it assumes when in vapour, and may be washed out of the receiver with water.

Instead of using the entire saline contents of kelp, the solution may be boiled down and crystallized, and the mother water of these first crystals, separately evaporated to dryness, will yield the iodine more abundantly than the whole salt. Neither the first crystals of the solution

of kelp, nor the residue insoluble in water, will afford any iodine.

Iodine is an opaque shining solid, permanent at a moderate temperature. When heated to about the temperature of boiling water it totally evaporates, forming a beautiful violet coloured vapour, which immediately again condenses unchanged on the cooler part of the vessel.

The chemical properties of iodine hitherto discovered are very curious. It possesses in a high degree the electrical properties of oxygen and oxymuriatic acid, and when combined with hydrogen it forms a peculiar *acid* very soluble in water, capable of assuming the gaseous form, and bearing the same relation to iodine that muriatic acid does to chlorine. The action of the different reagents on iodine will be the easiest understood by the reader by bearing this relation in mind.

When dry iodine and phosphorus are placed in contact, a reddish-brown substance is produced, and no gas is given out. When just moistened, copious acid fumes appear, which form a permanently elastic acid gas. The same acid is produced in liquid solution when the phosphorus and iodine are combined under water. In either case phosphoreous acid is generated, together with the peculiar acid of iodine. If the iodine much exceeds the phosphorus, a red insoluble compound of the two is produced, but when the proportions are properly adjusted, the whole resolves into a limpid acid

liquid, containing only phosphoreous acid and the acid of iodine dissolved in water. These may be separated by distillation. The first liquor that condenses is mere water, but when the contents of the retort become very concentrated, the acid of iodine distills over, and at last only phosphoreous acid remains, which gives out abundance of phosphuretted hydrogen.

This may be explained on Sir H. Davy's theory, by supposing that dry phosphorus and iodine simply combine into a compound analogous to that of phosphorus and chlorine; but when water is present it is decomposed, its oxygen acidifying the phosphorus, and its hydrogen acidifying the iodine in the same way as hydrogen is supposed to convert chlorine into muriatic acid.

The acid of iodine when gaseous is without colour, has nearly the smell of muriatic acid, smokes when exposed to the air, is rapidly absorbed by water, and gives a beautiful purple vapour with oxymuriatic gas. This acid gas when shaken with mercury is speedily and totally decomposed, a greenish-yellow substance similar to the compound of iodine and mercury is formed, and hydrogen is evolved equal in volume to half the acid gas.

Iron and zinc produce a similar effect.

The liquid acid of iodine obtained by dissolving the gas in water is a dense fluid, not very volatile, which rapidly decomposes the alkaline carbonates, dissolves iron and zinc with disengagement of hydrogen, but does not attack mercury even when heated, forms a soluble salt with barytes, and a red precipitate with corrosive sublimate. Heated with the black oxyd of manganese, with minium, or with the brown

oxyd of lead, it so far reduces these oxyds as to bring them to a state of solubility in acids, and iodine is disengaged. This partial reduction of the oxyds and total reduction of the acid of iodine appears therefore to be owing to the transfer of the hydrogen of the latter acid to the metallic peroxyd and consequent production of an equivalent portion of water. The red oxyd of mercury however does not regenerate iodine. When this acid is dissolved in water and exposed to galvanic action, iodine appears at the positive pole. The acid of iodine is not readily expelled from its compounds in its acid state. Thus when sulphuric acid is added to the salt formed by acid of iodine and potash, iodine alone is disengaged, and sulphureous acid unites with the alkali.

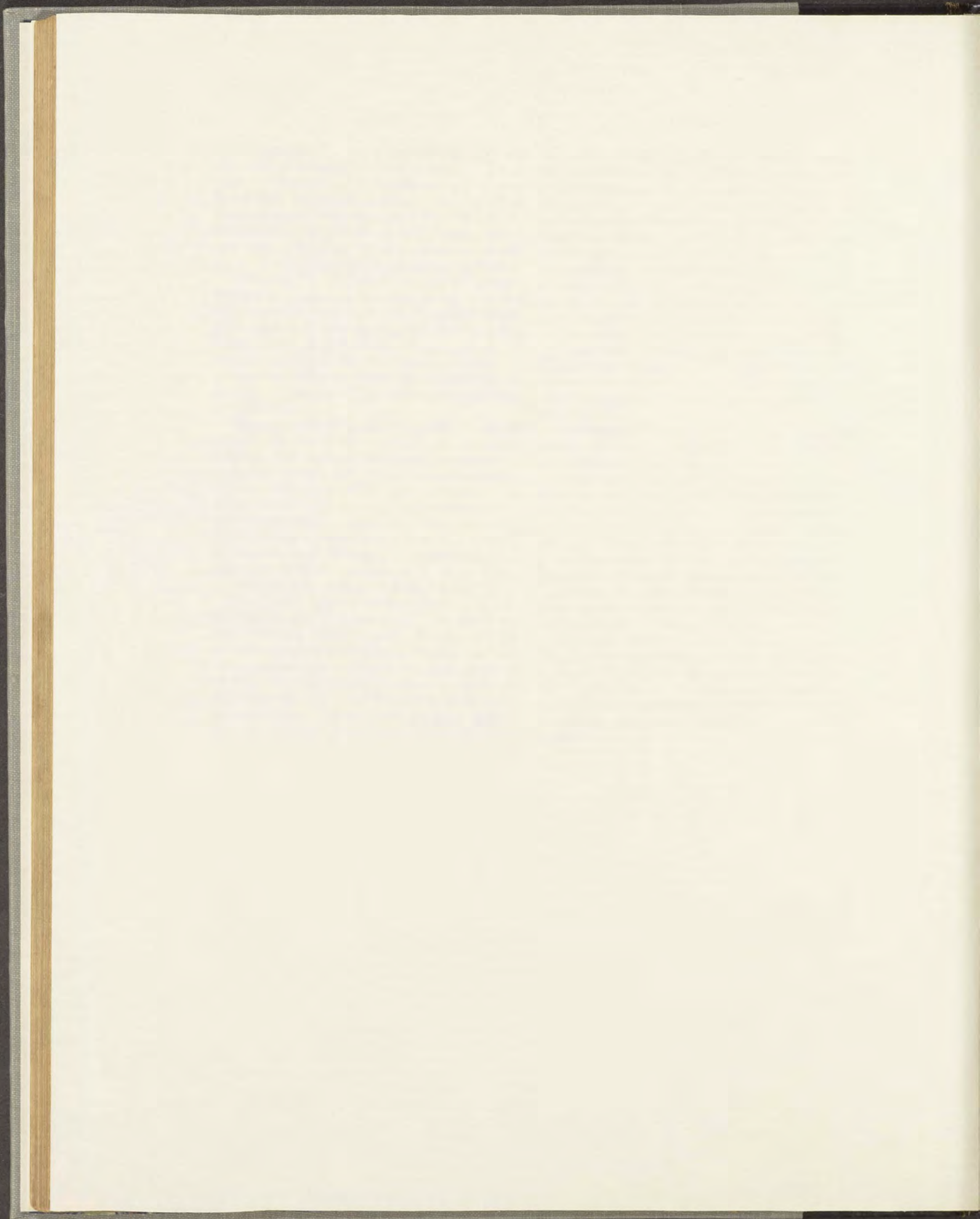
Sulphuretted hydrogen speedily deprives iodine of its colour, converts it to acid of iodine, and sulphur is deposited.

Iodine does not decompose water at any temperature. It combines with most metals without disengaging any gas. It dissolves in about a fifth of its weight of zinc. When this compound is heated under water nothing is disengaged, but a limpid solution is gradually formed, from which the alkalies separate an oxyd of zinc. Part of the water therefore appears to have been decomposed, its hydrogen acidifying the iodine, and its oxygen oxydating the zinc.

All these phenomena may be explained, as Dr. T. observes, either by supposing iodine to be an element and to form an acid by combining with hydrogen: or by supposing the acid of iodine to be a compound of water and an unknown base, and iodine to be this base united to oxygen.

*F I N I S.*







JOHN SINKANKAS  
5372 VAN NUYS COURT  
SAN DIEGO, CALIF. 92109

